Temperature-dependent orbital physics in a spin-orbital-lattice-coupled 2p electron Mott system: The case of KO2

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We have investigated the temperature (T)-dependent evolution of orbital states in a typical spin-orbital-lattice-coupled 2p electron Mott system KO2, based on the electronic structures obtained by the dynamical mean-field theory as well as the density functional theory. We have shown that KO2 exhibits the orbital fluctuation feature at high T due to degenerate πσ orbitals. Upon cooling, the orbital fluctuation is suppressed by the Jahn-Teller-type crystal field that becomes stronger with the lowering of structural symmetry, and then the ferro-orbital (FO) ordering emerges at low T. This FO ordering feature distinguishes KO2 from RbO2 and CsO2 in that the latter two seem to have antiferro-orbital orderings at low T, indicating that the underlying physics is different between them. We propose that the suppression of the orbital fluctuation in KO2 can be observed by thermal-conductivity measurement, as observed in spin-orbital-lattice-coupled 3d transition-metal oxides such as LaVO3.

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The spin-orbital-lattice coupling in transition-metal Mott insulators having degenerate 4 orbitals has been intensively investigated over the last decade [1–7]. According to their ground-state electronic structures, the degenerate 4 orbitals systems can be classified into three categories. In the first category, the orbital degeneracy is lifted by the crystal field (CF), such as the Jahn-Teller (JT) effect and the hybridization with cations. The orbital polarization initially driven by the CF is stabilized further by the strong Coulomb correlation. Then the resultant orbital ordering determines the magnetic interaction. In the second category, the superexchange interaction of the Kugel-Khomskii (KK) type induces the orbital and magnetic orderings. Here the CF plays a secondary role in stabilizing the orbital ordering. In the third category, the orbital fluctuation exists in the degenerate orbitals, for which the relativistic spin-orbit coupling (SOC) becomes effective in determining the magnetic interaction.

It is interesting that the spin-orbital-lattice coupling exists also in 2p electron systems, such as AO2 (A = Na, K, Rb, and Cs) alkali superoxides [8–16] and dioxygenyl O2PtF6 [17]. There are O2− anions in the former, while there are O2+ cations in the latter. As shown in Fig. 1(a), AO2 consists of alkali A+ cations and O2− molecule anions, and there are three electrons in the fourfold degenerate πσ orbitals. Hence, the orbital degeneracy occurs in a superoxide ion with 1 μB magnetic moment. According to the electron paramagnetic resonance (EPR) experiment, KO2 has different crystal structures depending on temperature (T) [18,19]. For T > 200 K, it has the CaC2-type tetragonal structure with the O2 molecular axis along the z direction [T structure in Fig. 1(a)]. Upon cooling, the O2 molecular axes in KO2 rotate coherently. They rotate first around the [100] direction so as to have the rotation angle θ of 20° for 10 < T < 200 K, which is denoted by the R[100] structure in Fig. 1(b). For T < 10 K, they rotate around the [110] direction to have θ = 30°, denoted by the R[110] structure in Fig. 1(c) [20]. At this T, the antiferromagnetic (AFM) spin ordering emerges simultaneously [18–20]. In the AFM structure, the magnetic moments of O2− anions are ferromagnetically aligned in the (001) plane, while they are antiferromagnetically aligned along the c direction [23].

Distinct from KO2, RbO2 and CsO2 have rather small rotation angles, θ < 5°, in the whole T range. Namely, instead of the coherent rotation of O2 molecular axes, the slight monoclinic and orthorhombic distortions occur for RbO2 and CsO2, respectively, upon cooling [14,18]. For RbO2, the AFM structure has not been observed, while, for CsO2, the one-dimensional (1D) AFM spin ordering, which is induced by the preexisting orbital ordering, has been observed [14].

There have been quite a few reports on the spin-orbital-lattice coupling in AO2 superoxides [8–16]. Magnetic interactions in relation to crystal structure variation in KO2 were discussed both experimentally [18,19] and theoretically [8]. Orbital states of KO2 at high- and low-T crystal structures were also investigated by using the density functional theory (DFT) [10]. However, the investigation of the T-dependent evolution of electronic structures and orbital states in AO2 in relation to the lowering of structural symmetry is still lacking.

In this Rapid Communication, we have explored T-dependent orbital states of KO2 based on the electronic structures obtained by using the dynamical mean-field theory (DMFT) as well as the DFT. Orbital states of KO2 at finite T are resolved in our study. We have demonstrated that the orbital fluctuation present at high T becomes completely suppressed upon cooling due to the lowering of structural symmetry. Then the AFM spin ordering occurs concomitantly with the emergence of the ferro-orbital (FO) ordering, which is driven by the CF of JT-type symmetry lowering. We have also shown that the situation in KO2 is far different from those in RbO2 and CsO2, for which the CF due to the O2 molecular axis rotation is not strong enough to induce the FO ordering.

For the DFT band-structure and total-energy calculations, we employed the full-potential augmented plane-wave band method implemented in the wien2k package [24,25]. We used the generalized gradient approximation (GGA) with incorporations of the SOC interaction and the on-site Coulomb interaction U of oxygen 2p electrons (DFT + U + SOC) [26]. We considered U values between 4 and 10 eV. We used 200 k points for the integration of the Brillouin zone [27]. We initialized the orbital density matrix to describe a specific orbital state. We used experimental lattice parameters a = 4.030 Å and c = 6.697 Å, and the bond length doo = 1.306 Å [19].
FIG. 1. (Color online) (a) Tetragonal (T) structure of KO₂, stable for T > 200 K. (b) R[100] structure of KO₂, stable for 10 < T < 200 K, in which O₂ molecular axes rotate coherently around θ |100| direction (θ ≈ 20°). (c) R[110] structure of KO₂, for T < 10 K, in which O₂ molecular axes rotate coherently around the [110] direction (θ ≈ 30°). This phase has simultaneous AFM and ferro-orbital (FO) orderings. (d) Schematic energy diagram showing electron occupation in a superoxide ion. Δ₇₂, Δ₉₉, and Δ₈₉ represent the crystal field (CF) gap, Kagel-Khomskii (KK) gap, spin-orbit coupling (SOC) gap, and Mott-Hubbard gap, respectively. The magnitude of Δ₉₉ is ∼20 meV [8]. (e) Δ₇₂ with variations of θ for R[100] and R[110] KO₂. Δ₇₂ increases monotonically with θ. (f) Δ₉₉ vs θ for R[110] KO₂. Δ₉₉ can be obtained by the total-energy difference between the AFM and FM states per formula unit, which corresponds to 4Jₜₐ. Here, Jₜₐ represents the effective interplane superexchange interaction between two superoxide ions. The DFT + U + SOC calculations with various U values were employed. (g) Δ₉₉ − Δ₉₉ vs θ for R[110] KO₂. KK inside the figure represents the KK-type quantum superexchange interaction dominant regime, while CF represents the classical CF dominant regime.

To obtain T-dependent electronic structures of strongly correlated 2p electrons in KO₂, we performed the DMFT calculations [28]. We have considered only the partially filled π⁺ orbitals for the DMFT calculation. The total bandwidth (W) of π⁺ orbitals is obtained to be ∼1 eV from the DFT calculation. We have determined the noninteracting part of the Hamiltonian using the downfolding scheme of Kohn-Sham DFT orbitals in the maximally localized Wannier function (MLWF) basis [29].

The interacting part of the Hamiltonian is given by

\[ H_I = U \sum_{m,R} n_{m,R,\uparrow} n_{m,R,\downarrow} + U' \sum_{m>R,R'} n_{m,R,\sigma} n_{m,R',\bar{\sigma}} + (U' - J) \sum_{m>R,R',\sigma} n_{m,R,\sigma} n_{m,R',\bar{\sigma}}, \]

where U, U', and J are the intra- and interorbital Coulomb correlation, and the Hund interaction parameters, respectively. \( n_{m,R,\sigma} \) represents the occupation number at orbital m, site R, and spin \( \sigma \). We considered here the rotationally symmetric interaction, so that \( U' = U - 2J \). We used interaction parameters of \( U = 3.55 \) eV and \( J = 0.62 \) eV, which were obtained by a constrained local-density approximation and random-phase approximation [8]. Thus, in view of \( U/W > 1 \), KO₂ is in the Mott insulator regime, as will be discussed further. We used the continuous time quantum Monte-Carlo (CTQMC) method as an impurity solver [30,31].

As shown in Fig. 1(d), the orbital degeneracy of the π⁺ level in KO₂ is to be lifted either (i) by the CF due to coherent rotation of superoxide ions, (ii) by the quantum superexchange interaction of the KK type, or (iii) by the intrasite SOC. The CF acts like a JT effect to make the π⁺ orbital have higher energy than the π⁻ orbital with the energy gap of Δ₇₂. The KK-type superexchange would lift the degeneracy of the π⁺ level with preference of electron delocalization along the orbital order by the energy gap of Δ₉₉. The intrasite SOC would split the degenerate π⁺ level into π⁺_m = 1 and π⁺_m = -1 orbitals with an energy gap of Δ₈₉ (∼20 meV) [8,10]. In reality, the relative magnitude of Δ₇₂, Δ₉₉, and Δ₈₉ would determine the splitting mechanism of the π⁺ level in KO₂. Then, the partially filled π⁺ orbitals are split further by the Coulomb repulsion to exhibit the Mott-Hubbard gap (Δ₈₉). Using the DFT + U + SOC, we have obtained that Δ₈₉ is between 0.24 and 1.20 eV, confirming the Mott insulating state of KO₂. This Mott insulating state is consistent with our DMFT result below.

Let us compare the relative magnitude of Δ₇₂ and Δ₉₉, for R[110] KO₂. Figure 1(e) presents Δ₇₂ as a function of rotation angle θ, which is obtained by the on-site noninteracting part of the Hamiltonian in the MLWF basis. Δ₇₂ increases monotonically with θ for both rotations around the [100] and [110] axes, implying that the JT-type CF generates the π⁺-hole FO ordering at low T. Note that Δ₉₉ corresponds to the superexchange energy gain per superoxide ion, which can be estimated by the total-energy difference (4Jₜₐ) between the AFM and ferromagnetic (FM) states of R[110] KO₂ assuming π⁺-hole FO order [32]. Here, Jₜₐ represents the effective interplane superexchange interaction strength between two superoxide ions. Figure 1(f) shows Δ₉₉ as a function of θ, which shows that the AFM phase becomes more stable for θ > 5° in R[110] KO₂.

In Fig. 1(g), we compare the Δ₇₂ and |Δ₉₉| values as a function of θ for R[110] KO₂. For θ < 10°, Δ₇₂ − |Δ₉₉| is negative, which implies that the KK-type quantum superexchange effect dominates over the CF effect. In this regime, Δ₉₉ has a comparable magnitude to Δ₉₉ (∼20 meV). As a result, the orbital ordering in this regime is driven by the competing superexchange interaction and SOC. In contrast, for θ > 10°, Δ₇₂ − |Δ₉₉| becomes positive, which implies that the classical JT-type CF is dominating. In this regime, Δ₇₂ is larger than Δ₉₉. As a result, the orbital ordering is driven solely by the CF. At θ = 10°, the Δ₇₂ − |Δ₉₉| value is close to zero, which indicates the competition of two mechanisms.

We have performed the DMFT calculations to obtain finite-T electronic structures of KO₂ for different crystal structures. Figure 2 presents the imaginary parts of Green’s functions and self-energies for π⁻ and π⁺ orbitals of KO₂ at room temperature (T = 300 K). The imaginary part of the Green’s function for each structure has zero value and negative derivative at \( \omega_n = 0 \) (\( \omega_n \): Matsubara frequency), implying that KO₂ is an insulator at room temperature. The imaginary parts of self-energies for the
\( \pi_x \) and \( \pi_y \) orbitals have similar values for \( \theta = 0^\circ \). In contrast, the imaginary part of self-energy for the \( \pi_y \) orbital is much larger than that of \( \pi_x \) near \( \omega_n = 0 \) for \( \theta = 30^\circ \) of both the R[100] and R[110] structures. This behavior of self-energies suggests that there exists an orbital fluctuation at \( \theta = 0^\circ \), but this orbital fluctuation is suppressed with the emergence of \( \pi_y \)-hole FO ordering for \( \theta = 30^\circ \) structures. This feature will be seen more clearly in Fig. 3 below.

On the basis of the DMFT results, we have obtained the orbital state phase diagram with respect to \( T \) and the crystal structure of KO\(_2\). Figure 3 presents \( T \)-dependent orbital polarization for each rotated structure. We define the orbital polarization as \( P = (P_{\pi_y} - P_{\pi_x})/(P_{\pi_y} + P_{\pi_x}) \), where \( P_{\pi_x} \) indicates the probability of a \( \pi_x \)-hole orbital state in the DMFT calculation. For small rotation (\( \theta \leq 5^\circ \)) in Fig. 3(a), the orbital polarization \( P \) is close to zero for \( T > 100 \) K, which indicates that the orbital state of KO\(_2\) is disordered at high \( T \). This feature is consistent with the orbital fluctuation feature, as discussed in Fig. 2 for \( \theta = 0^\circ \). With lowering \( T \) below 100 K, we observed the irregular oscillation between \( P_{\pi_x} \) and \( P_{\pi_y} \) during iterations of the self-consistency loop, which reveals the complex orbital state in this regime. One possible candidate state in this regime would be the antiferro-orbital (AFO) ordering state, as suggested for RbO\(_2\) and CsO\(_2\) [15], in which \( \theta \) are smaller than 5° [14,18]. As discussed in Fig. 1(g), for small \( \theta \), the KK-type superexchange effect dominates over the CF effect. The signature of AFO ordering in this regime indicates that the orbital order is driven by the quantum superexchange interaction rather than the classical CF. In other words, the absence of the FO ordering in RbO\(_2\) and CsO\(_2\) can be understood in terms of their small rotation angles, which do not produce strong enough CF to generate the FO ordering.

For large rotation angles (\( \theta > 10^\circ \)) in Fig. 3(b), the full orbital polarization is achieved around 100 K with the suppression of the orbital fluctuation. This result indicates that, in KO\(_2\), the AFM spin ordering at low \( T \) is realized with the emergence of FO ordering. At large \( \theta \), the CF effect dominates over the superexchange effect, whereby the \( \pi_x \)-hole FO ordering emerges in the large rotation structures. At \( \theta = 10^\circ \), these two mechanisms compete. As a result, it is seen in Fig. 3(b) that the \( \pi_x \)-hole FO ordering occurs only at very low \( T \) of \( \sim 20 \) K.

Notice that the orbital fluctuation in the rare-earth vanadates, such as LaVO\(_3\), was characterized by the glassy behavior of thermal conductivity [1,4,33]. In LaVO\(_3\), the thermal conductivity becomes much reduced due to scattering of phonons by disordered orbital states. According to the phase diagram in Fig. 3(a), such orbital fluctuation exists in KO\(_2\) at room-temperature \( T \). Then we expect the suppression of thermal conductivity in KO\(_2\) due to this orbital fluctuation. The comparison of the thermal conductivities between KO\(_2\) and peroxide BaO\(_2\) that has fully occupied \( \pi_x^* \) orbitals would give great insight into the orbital fluctuation effect in KO\(_2\) [34]. Further, if the orbital fluctuation is suppressed upon cooling, the thermal conductivity of KO\(_2\) would be recovered from the glassy behavior to become close to that of BaO\(_2\). In fact, the suppression of orbital fluctuation with rotation of \( \pi_x \)-hole anion axes was recently observed in Cs\(_2\)O\(_6\), which has mixed valences of closed-shell peroxide \( \text{O}_2^{2-} \) and open-shell superoxide \( \text{O}_2^{-} \) anions [35].

To examine the possible orbital state for small \( \theta \) and to confirm that the \( \pi_x \)-hole FO order is compatible with the observed AFM structure for large \( \theta \), we have performed total-energy calculations in the DFT + \( U \) + SOC for various orbital states. We have obtained at \( \theta = 0^\circ \) that KO\(_2\) has the stable \((x+y, x-y)\)-hole AFO ordering state (see Fig. S2 in the Supplemental Material [32]). Here, the \((a,b)\)-hole state represents the \( \pi_x \) and \( \pi_y \)-hole orbital states for two superoxide ions in the \((1 \times 1 \times 1)\) tetragonal unit cell [32]. Directional coordinates for \((a,b)\) are depicted in Fig. 1. Noteworthy is that the SOC is known to play an important role in the ground state of KO\(_2\) at \( \theta = 0^\circ \) [8,10]. \( \Delta_{SO} \) in KO\(_2\) is as much as \( \sim 20 \) meV [8], and the large orbital moment was.
Indeed observed in isolated superoxides [36]. As mentioned earlier, $\Delta_{SO}$ and $\Delta_{KK}$ have comparable magnitude at $\theta = 0^\circ$, suggesting the competition between the superexchange-driven AFO order and the SOC-driven $\pi^+\_hole$ level splitting. Actually, we have confirmed that the SOC-induced state with azimuthally symmetric hole orbital shape has a comparable total energy to the $(x+y, x-y)$-hole state [32,37].

This result for $\theta = 0^\circ$ corroborates our earlier finding that the FO order will not be realized in superoxides having small rotation angle $\theta$. RbO$_2$ and CsO$_2$ have $\theta \approx 0^\circ$. For RbO$_2$, the emergence of in-plane AFO ordering with cation distortions was reported [11,13,14]. For CsO$_2$, there was a report that the high-$T$ phase exhibits the Curie-Weiss magnetic susceptibility with large orbital moment contribution, while the low-$T$ phase exhibits the in-plane AFO order with superexchange interaction and cation distortion [14]. Therefore, distinct from KO$_2$ which has the dominant CF effect, RbO$_2$ and CsO$_2$ have the interplay between various interaction effects including the KK-type superexchange, the SOC, and the cation distortion. As shown in Fig. 4, for the given experimental AFM structure of KO$_2$, only the R[110] structure has the stable $\pi^+_\_hole$ FO $(y,y)$ state at finite $\theta \sim 30^\circ$, as is consistent with the DMFT result of Fig. 3(b). In contrast, the R[100] structure in Fig. 4(a) does not favor the $\pi^+_\_hole$ FO state at $\theta \sim 30^\circ$ because the FO $(y,y)$ state tends to induce the AFM interaction along the [010] direction that is not compatible with the experimental AFM structure. This result is consistent with that of Ref. [10] and the observed phase diagram at low $T$. It thus suggests that the structural transition from R[100] with $\theta = 20^\circ$ to R[110] with $\theta = 30^\circ$ at 10 K occurs through the strong connection between the FO ordering and the AFM transition.

In conclusion, we have investigated $T$-dependent orbital states and magnetism of KO$_2$ based on the DFT and DMFT calculations. At high $T$, KO$_2$ exhibits the orbital fluctuation. Upon cooling, the FO state emerges with the large coherent rotation of superoxide ions and the corresponding enhancement of the JT-type CF. This FO state is compatible with the observed AFM spin ordering at low $T$ only for the rotation around the [110] axis. In RbO$_2$ and CsO$_2$, the rotation angle is inherently too small to generate the FO ordering. Instead, in RbO$_2$ and CsO$_2$, the AFO ordering occurs through the interplay between various interaction effects including the KK-type superexchange, the SOC, and cation distortion. The suppression of the orbital fluctuation at room temperature can be probed from the comparative measurements of thermal conductivities for KO$_2$ and BaO$_2$.

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[20] There were theoretical predictions for the zero-$T$ crystal structure of KO$_2$ [12,21,22], which are different from that of Fig. 1(c). In fact, the predicted crystal structures are different between Ref. [12] and Refs. [21,22], even though these reports were from the same group. This inconsistency indicates that more elaborate theoretical studies on the crystal structure of KO$_2$ are demanded.
[27] The convergence of the total-energy difference between different electronic structures was checked down to 7 meV per formula unit.
[34] W. Wong-Ng and R. S. Roth, Physica C 233, 97 (1994).
[37] We have confirmed that the SOC-induced state with spin direction along [001] has a comparable energy to the \((x + y, x - y)\)-hole state. In the electron paramagnetic resonance (EPR) experiment at \(T < 200 \text{ K}\), the spin direction was found to be normal to the molecular direction [18].