Rubidium superoxide: a \( p \)-electron Mott insulator

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Rubidium superoxide, \( \text{RbO}_2 \), is a rare example of a solid with partially-filled electronic \( p \) states, which allows to study the interplay of spin and orbital order and other effects of strong electronic correlations in a material that is quite different from the conventional \( d \) or \( f \) electron systems. Here we show, using a combination of density functional theory (DFT) and dynamical mean-field theory, that at room temperature \( \text{RbO}_2 \) is indeed a paramagnetic Mott insulator. We construct the metal-insulator phase diagram as a function of temperature and Hubbard interaction parameters \( U \) and \( J \). Due to the strong particle-hole asymmetry of the \( \text{RbO}_2 \) band-structure, we find strong differences compared to a simple semi-elliptical density of states, which is often used to study the multiband Hubbard model. In agreement with our previous DFT study, we also find indications for complex spin and orbital order at low temperatures.

I. INTRODUCTION

Rubidium superoxide, \( \text{RbO}_2 \), is an interesting example of a material, where spin and orbital order appears not as a result of partially filled \( d \) or \( f \) states, but due to partially filled \( p \) electron states. \( \text{RbO}_2 \) is a member of the family of alkali superoxides \( \text{AO}_2 \) (\( A = \text{K}, \text{Rb}, \) or \( \text{Cs} \)), which are insulating crystalline materials composed of \( A^+ \) and \( (\text{O}_2)^- \) ions. At room temperature, \( \text{RbO}_2 \) has a tetragonal crystal structure (see Fig. 1(a)), while with decreasing temperature this structure undergoes several weak distortions, first to orthorhombic, then to monoclinic symmetry. The electronic structure around the Fermi level is dominated by oxygen \( p \) states which can be well approximated by molecular orbitals (MOs) corresponding to the \( \text{O}_2 \) units, and are filled with 9 electrons (see Fig. 1(b)). Assuming no further symmetry breaking, the two highest occupied antibonding \( \pi^* \) orbitals are \( 3/4 \) filled.

The degeneracy of these orbitals can be lifted through either magnetic or orbital long range order, or both. The alkali superoxides thus allow to study “correlation effects” in a completely different class of materials compared to the more conventional transition metal oxides or \( f \) electron systems. Antiferromagnetic order is indeed found experimentally at low temperatures \( (T_N(\text{RbO}_2) \approx 15 \text{ K}) \), and it was suggested by recent density functional theory (DFT) and model studies that the insulating character of alkali-superoxides at low temperatures can be explained by the interplay of correlation effects (spin and orbital order) and crystal distortions. However, the nature of the insulating state of these superoxides at room temperature has so far remained unexplored.

Due to the high symmetry crystal structure with no long-range order of spins or orbitals, it is impossible to explain the insulating character of the alkali superoxides at room temperature within an effective single particle band picture. Here we show, using a combination of DFT and dynamical mean field theory (DFT+DMFT), that \( \text{RbO}_2 \) at room temperature is in fact a Mott insulator, where the strong Coulomb repulsion prevents the electron hopping between adjacent sites.

II. ELECTRONIC STRUCTURE OF \( \text{RbO}_2 \)

We obtain the electronic structure of \( \text{RbO}_2 \) from a non-spinpolarized DFT calculation using the Quantum-Espresso package, employing the generalized gradient approximation of Perdew, Burke, and Ernzerhof, and ultrasoft pseudopotentials. Figs. 2(a) and (b) show the resulting density of states (DOS) and bandstructure. It can be seen that the electronic structure of \( \text{RbO}_2 \) indeed closely resembles the simple MO picture sketched in Fig. 1(b), with a splitting of about 5 eV between the bonding and antibonding \( \pi \) and \( \pi^* \) bands, and a single band corresponding to bonding \( \sigma \) MOs at \(-6 \text{ eV}\). The antibonding \( \sigma^* \) states at \( \sim 5 \text{ eV} \) are strongly intermixed with other empty states corresponding to the

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![Figure 1](image-url)

**FIG. 1:** (a) Tetragonal crystal structure of \( \text{RbO}_2 \) at room temperature. (b) Electronic structure represented by a set of oxygen \( p \) molecular orbitals.
Rb$^+$ cations.

III. DYNAMICAL MEAN-FIELD THEORY — COMPUTATIONAL METHOD

To calculate the electronic properties at finite temperature and account for local correlation effects, we use dynamical mean-field theory (DMFT) which allows to map the lattice problem to an effective problem of a single-site impurity surrounded by a bath. The interaction part of the impurity Hamiltonian is taken to be of the Slater-Kanamori form

$$H_{\text{int}} = \sum_a U_n a^\dagger a + \sum_{a \neq b, \sigma} U' n_a, \sigma n_{b, -\sigma}$$

$$+ \sum_{a \neq b, \sigma} (U' - J) n_a, \sigma n_{b, \sigma}$$

$$- \sum_{a \neq b} J (d^\dagger_{a, \sigma} d^\dagger_{b, \sigma} d_{b, \sigma} + d^\dagger_{b, \sigma} d^\dagger_{a, \sigma} d_{a, \sigma} + h.c.),$$

with $d^\dagger_{a, \sigma}$ the creation operator for an electron of spin $\sigma$ in orbital $a$ and $U' = U - 2J$. To solve the effective impurity problem, we use the strong-coupling continuous time quantum Monte Carlo approach (CT-HYB\textsuperscript{14,15}. From the self-consistently determined hybridization function $\Delta(\tau)$, the impurity Green’s function $G_{\text{imp}}(\tau)$ is computed and measured on a homogeneous grid of $N_\tau = 1000 \sqrt{\beta/40 \text{ eV}^{-1}}$ points, where $[\ldots]$ represents the nearest integer number. After Fourier transformation we obtain the self-energy in Matsubara space,

$$\Sigma(i\omega_n) = i\omega_n + \mu - G_{\text{imp}}^{-1}(i\omega_n) - \Delta(i\omega_n),$$

where $\omega_n = (2n + 1)\pi/\beta$ for integer $n$, $\mu$ is the chemical potential, and $\beta = 1/T$ the inverse temperature. Using this self-energy and the single-particle Hamiltonian $H(k)$ we obtain the local lattice Green’s function by averaging over the Brillouin zone:

$$G_{\text{loc}}(i\omega_n) = \frac{1}{N_k} \sum_k [\omega_n + \mu - H(k) - \Sigma(i\omega_n)]^{-1}.\quad(3)$$

The DMFT self-consistency condition demands that this local lattice Green’s function is the same as the impurity Green’s function. This condition, in combination with Eq. (2) yields the hybridization function for the next DMFT iteration,

$$\Delta(i\omega_n) = i\omega_n + \mu - G_{\text{loc}}^{-1}(i\omega_n) - \Sigma(i\omega_n).\quad(4)$$

We only include the partially-filled antibonding $\pi^*_{x/y}$ bands in our DMFT calculations for RbO$_2$, and express the corresponding Hamiltonian $H(k)$ in a basis of maximally localized Wannier functions\textsuperscript{16}. The corresponding DOS is shown in Fig. 2(c). One can recognize a pronounced asymmetry with respect to half-filling. In DMFT studies, a model semicircle (SC) density of states (DOS) is often employed to represent the electronic bands, since it leads to a simple expression connecting $\Delta$ and $G_{\text{imp}}$. Furthermore, due to the resulting particle-hole symmetry, only occupations between zero and half-filling need to be studied. Here, we investigate the differences between results obtained using the model SC DOS and the realistic DFT band structure of RbO$_2$ in the tetragonal crystal structure. The bandwidth of the SC DOS is set equal to the bandwidth of the RbO$_2$ DOS (0.93 eV, see Fig. 2(c)).

IV. RESULTS

A. Room temperature properties

Generally, the value of the spectral function at zero energy indicates whether a material is insulating or metallic. However, obtaining the spectral function from the imaginary time Green’s function requires an analytic continuation to the real axis, which can introduce additional uncertainties\textsuperscript{17}. We therefore consider several possible indicators for the metal-insulator transition (MIT) which are directly accessible from $G_{\text{imp}}(\tau)$. All of these quantities (described in more detail below) are compared in Fig. 3 calculated at room temperature ($\beta = 40 \text{ eV}^{-1}$) for interaction parameters close to the MIT ($U = 1.2 \text{ eV}$ and $J = 0$).

One possibility is to monitor the occupation $n = -\sum_\alpha G_{\text{imp}}^\alpha(\beta)$ ($\alpha$ is the spin-orbital index) as a function of the chemical potential $\mu$ (see Fig. 3(a)) and
to identify the insulating phase by a plateau in $n(\mu)$. This, however, requires a large number of calculations for slightly different values of $\mu$. Another indicator is given by the mass enhancement in the low-temperature metallic phase, which grows rapidly as the Mott insulating state is approached, and which we estimate from the self-energy at the lowest Matsubara frequency (see Ref. [18]):

$$\left\{ m^* \right\}_{\text{est.}} = 1 - \frac{3|\Sigma(\omega_0)|}{\omega_0}.$$  \hfill (5)

We also consider the following estimate of the spectral function (see e.g. Ref. [18]):

$$A(0) \approx -\frac{\beta}{\pi} G_{\text{imp}} \left( \frac{\beta}{2} \right).$$  \hfill (6)

While for both of these quantities (shown in Fig. 3(b) and 3(c), respectively) only one calculation at the correct $\mu$ value is required, the identification of the MIT phase boundary requires the definition of a suitable threshold value. In addition, $G(\beta/2)$ suffers from significant statistical noise in the insulating state, as this $\tau$-region is difficult to sample with standard CT-HYB. A quantity which is quite insensitive to noise is the slope of $G_{\text{imp}}(\omega \to 0)$, which is positive/negative for the metallic/insulating state [13]. In practice, we estimate the slope $K$ from $G_{\text{imp}}(\omega)$ at the two lowest Matsubara frequencies:

$$K = \left\{ \frac{d\Im[G_{\text{imp}}(0)]}{d\omega} \right\}_{\text{est.}} = \frac{\Im[G_{\text{imp}}(\omega_1) - G_{\text{imp}}(\omega_0)]}{\omega_1 - \omega_0}. $$  \hfill (7)

In Fig. 3, a clear difference can be seen between the SC and the RbO$_2$ input. For the SC, the insulating state already appears at 1 and 3 el filling, while 2 el filling is clearly metallic. In contrast, the RbO$_2$ electronic structure yields a clear insulating state at 3 el filling and a (just barely) insulating state at 2 el filling, while 1 el filling is still metallic. The different range of $\mu$ which leads to the insulating state for SC and RbO$_2$, respectively, indicates a sizable shift of the corresponding MIT boundary. The particle-hole asymmetry in the real electronic structure of RbO$_2$ thus leads to large quantitative changes compared to the simple SC DOS.

Fig. 4 shows the slope $K$ for different values of $U$ and $J$ at $T \approx 290$ K using the RbO$_2$ band structure. For fixed $J = 0$ eV, there is an obvious tendency towards the insulating state with increasing $U$ for all integer fillings, as expected. However, at fixed $U = 2$ eV, increasing $J$ favors the Mott insulator at half-filling (2 el) but favors the metallic solution for 1 and 3 el fillings. This is consistent with previous discussions of multi-orbital models [19,20]. In the large-$U$ limit, the width of the “Mott plateau” in $\mu$ is given by $\Delta_{\text{Mott}}^\text{est.} = E_{n+1} + E_{n-1} - 2E_n$, with $E_n$ denoting the lowest eigenvalue of the $n$-particle eigenstates of $H_{\text{int}}$ (Eq. (11)) [19]. In our two-orbital case this estimate yields $U - 3J$ for $n = 1, 3$ and $U + J$ for $n = 2$, in agreement with the observed dependence of the plateau-width on $J$. In reality, the Mott plateau will be reduced by approximately the bandwidth $W$, so that we obtain the rough estimate

$$\Delta_{\text{Mott}}^\text{est.} \approx U - 3J - W.$$  \hfill (8)

Based on the identification of the MIT boundary us-
Furthermore, the critical ary in Fig. 5(a) agrees nicely with this simple estimate. A crude estimate for the critical interaction strength:

\[ U \approx \frac{\Delta_{\text{Mott}}}{\text{const}} \]

must be larger than zero for a Mott insulating solution to exist, Eq. (8) also provides a clear gap in the spectral function, even at room temperature. To demonstrate this, we have used the maximum entropy method to construct spectral functions for realistic values of the interaction parameters \( U = 0.6 \text{ eV}, \) \( J = 0.6 \text{ eV}, \) and \( Z = (m^*/m) \) at \( \beta = 40 \text{ eV}^{-1} \) (Fig. 6(a)). A gap is present for \( U \geq 2.7 \text{ eV}, \) in perfect agreement with the various indicators of the MIT discussed previously (and which are shown in Fig. 6(b)). In agreement with Ref. 21 we find a “bad metal” region with a strongly renormalized \( Z = (m^*/m) \) in the vicinity of the Mott transition. From Fig. 6(a) it can be seen that this corresponds to spectral functions with substantial narrowing of the central quasiparticle feature and an emerging three-peak structure visible for \( U = 2.4 \text{ eV}. \) In addition, there is a significant spectral weight transfer to energies around \(-2 \text{ eV}\) compared to the noninteracting DOS.

B. Low temperature behavior

Finally, we focus on the low-temperature behavior. While for temperatures \( T \geq 200 \text{ K} \) (for which we didn’t find indications of ordered states), the hybridization function is averaged over all spin-orbitals in each iteration, Fig. 7 shows the evolution of the occupation of each individual spin-orbital at \( T \approx 29 \text{ K} \) when no such averaging is performed. While for some values of \( J \) the occupation eventually converges to spin and/or orbitally polarized states, the occupations exhibit characteristic oscillations for other values of \( J. \) As discussed in Ref. 22, such oscillations indicate that the system wants to adopt an ordered state with a sublattice structure that is incompatible with the applied self-consistency condition (in our case all sites are forced to be equivalent).

Even though we do not attempt to fully resolve the resulting spin and orbital patterns, we can make a number of interesting observations. First of all, there are drastic differences between RhbO\(_2\) (Fig. 4(a)) and the simple SC DOS (Fig. 7(b)). The latter oscillates between three states with different spin and orbital polarization (SP and OP) and is insulating for \( J \leq 0.8 \text{ eV}, \) while for higher \( J \) it is metallic with no SP and OP (in these calculations...
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FIG. 7: (Color online) Evolution of individual occupations for different \( J \) and fixed \( U - J = 2.93 \) eV at \( T \approx 29 \) K for RbO\(_2\) input (a) and for the SC DOS (b). (Black) Squares: orbital 1, spin up; (red) diamonds: orbital 2, spin up; (green) plus symbols: orbital 1, spin down; (blue) crosses: orbital 2, spin down.

FIG. 8: (a) Temperature dependence of spin and orbital polarization for fixed \( U \) and \( J \). (b) spin and orbital polarization as a function of \( J \) for \( U - J = 2.93 \) eV and \( T \approx 29 \) K. All data corresponds to RbO\(_2\) input.

both \( U \) and \( J \) have been varied while keeping \( U_{\text{eff}} = U - J \) constant. For RbO\(_2\) we can distinguish three different regimes (see Fig. 8(b)). For \( J \leq 0.5 \) eV, the occupation oscillates between three different states with different SP and almost no OP. For \( J = 0.62 \) and 0.8 eV, a stable solution with large OP and zero SP appears, while a further increase of \( J \) induces a stable SP and reduced OP. The system is insulating for all \( J \leq 1.0 \) eV, while for \( J = 1.2 \) eV it is a ferromagnetic half-metal with full SP and no OP. In Fig. 8(a) we show the SP and OP of RbO\(_2\) as a function of temperature for the realistic values \( U = 3.55 \) eV and \( J = 0.62 \) eV. The system is insulating and while essentially no SP develops down to \( T \approx 30 \) K, OP appears below \( T \approx 60 \) K and reaches almost its maximum at \( T \approx 30 \) K. While it is not possible from our calculations to make a prediction about the character of the expected spin- and orbitally-ordered ground state, the above temperatures are consistent with our previous estimate of the ordering temperature based on total energy differences of different orbitally ordered configurations obtained from DFT+U calculations at \( T = 0 \) K.

V. SUMMARY AND CONCLUSIONS

In summary our calculations clearly show that for realistic values of the interaction parameters \( U \) and \( J \), RbO\(_2\) at room temperature is a paramagnetic Mott insulator without exhibiting any symmetry-breaking long-range order. We find pronounced quantitative differences between the widely used SC DOS and the realistic electronic structure of RbO\(_2\), which leads to a strong asymmetry between the 1/4-filled and 3/4-filled cases. We also find indications of complex spin and orbital order below \( T \approx 30 \) K, the character of which seems to depend strongly on \( J \). Furthermore, at low temperature RbO\(_2\) exhibits clear qualitative differences compared to the simplified SC DOS. It will be interesting to clarify in future work whether single site DMFT is capable to resolve the complicated spin and orbital patterns predicted within model calculations based on a perturbative treatment of electron-electron interaction and a simplified electronic structure of RbO\(_2\).

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1. A. Zumsteg, M. Ziegler, W. Känzig, and M. Bösch, Phys. Condens. Matter 17, 267 (1974).
2. M. Labhart, D. Raoux, W. Känzig, and M. A. Bösch, Phys. Rev. B 20, 53 (1979).
3. M. Rosenfeld, M. Ziegler, and W. Känzig, Helv. Phys. Acta 51, 298 (1978).
4. I. V. Solovyev, New Journal of Physics 10, 013035 (2008).
5. R. Kováčik and C. Ederer, Phys. Rev. B 80, 140411 (2009).
6. M. Kim, B. H. Kim, H. C. Choi, and B. I. Min, Phys. Rev. B 81, 100409 (2010).
7. E. R. Ylvisaker, R. R. P. Singh, and W. E. Pickett, Phys. Rev. B 81, 180405 (2010).
8. A. K. Nandy, P. Mahadevan, P. Sen, and D. D. Sarma, Phys. Rev. Lett. 105, 056403 (2010).
9. K. Wohlfeld, M. Doghofer, and A. M. Oles, EPL 96, 27001 (2011).
10. P. Gianozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, et al., J. Phys.: Condens. Matter 21, 395502 (2009).
11. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
12. D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
13. A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996).
14. P. Werner and A. J. Millis, Phys. Rev. B 74, 155107 (2006).
15. E. Gull, A. J. Millis, A. I. Lichtenstein, A. N. Rubtsov, M. Troyer, and P. i. Werner, Rev. Mod. Phys. 83, 349 (2011).
16. A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comp. Phys. Comm. 178, 685 (2008).
17. M. Jarrell and J. E. Gubernatis, Phys. Rep. 269, 133 (1996).
18. S. Fuchs, E. Gull, M. Troyer, M. Jarrell, and T. Pruschke, Phys. Rev. B 83, 235113 (2011).
19. P. Werner, E. Gull, and A. J. Millis, Phys. Rev. B 79, 115119 (2009).
20. L. de’ Medici, Phys. Rev. B 83, 205112 (2011).
21. L. de’ Medici, J. Mravlje, and A. Georges, Phys. Rev. Lett. 107, 256401 (2011).
22. C.-K. Chan, P. Werner, and A. J. Millis, Phys. Rev. B 80, 235114 (2009).