Electronic structure of rare-earth binary oxide superconductor LaO

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Recently the superconductivity has been discovered in the rock-salt structured binary lanthanum monoxide LaO through the state-of-the-art oxide thin-film epitaxy. This work reveals the normal state of superconducting LaO to be a Z2 nontrivial topological metal that the Dirac point protected by the crystal symmetry is located at around the Fermi energy. By analysing the orbital characteristics, the nature of topological band structure of LaO originates from the intra-atomic transition in energy from outer shell La 5d to inner shell 4f orbitals driven by the strong octahedral crystal-field. Furthermore, the appearance of novel surface states unambiguously demonstrates the topological signature of LaO. Our theoretical findings not only shed light into the understanding of exotic quantum behaviors in LaO superconductor with intimate correlation between 4f and 5d orbitals in La, but also provide an exciting platform to explore the interplay of intriguing nontrivial topology and superconductivity.

Introduction. — The search for exotic quantum states in quantum materials is an appealing subject in condensed matter physics. Among them, rare-earth compounds possess their unique physical properties such as mixed-valence phenomena [1, 2], Kondo insulating states [3, 4], heavy-fermion behavior [5], and intriguing superconductivity [6]. Prominently, the rare-earth binary compound of lanthanum superhydride LaH10 under extreme high pressures displays the high transition temperature (Tc) superconductivity with Tc of 260 K towards the goal of achieving room-temperature superconductors [7, 8]. At ambient pressure, the binary lanthanum dicarbide LaC2 is also shown to become superconductivity at 1.6 K [9]. Compared with LaC2, the binary lanthanum sesquicarbide La2C3 has a superconducting Tc of 11 K [10, 11], which can be further enhanced to 13 K by tuning the La/C ratio [12]. The inherent pairing symmetry of these binary lanthanum carbide superconductors, however, needs further scrutiny [13].

Recently, a new type of binary lanthanum monoxide LaO with rock-salt structure was reported to be a superconductivity with Tc of 5 K through the advance in the state-of-the-art oxide thin-film epitaxy techniques [14], since the rare-earth elements usually prefer the trivalent ionic state to form the most stable binary sesquioxides [15], which are well-known high permittivity wide-gap insulators promising for gate dielectrics [16]. For metastable rare earth monoxides, the electronic properties are significantly different from those sesquioxides because of the presence of outer shell 5d conduction carriers in La atoms strongly interacting with their localized inner shell 4f electrons around the Fermi energy [17]. The electronic band structure calculations have been carried out to verify that the conducting electrons around the Fermi level in LaO superconductor mainly come from the contribution of La 5d orbitals hybridized strongly with the La 4f orbitals [18], implying the binary lanthanum monoxide superconductor LaO to impart the possibility of topologically nontrivial electronic structures driven by the La 5d-4f orbital transitions in energy with opposite parity.

In this paper, we revisit the nature of interplay between La 5d and 4f orbitals on the newly discovered rare-earth binary superconductor LaO based on the framework of the first-principles calculations, and find the normal state of LaO superconductor to be a nontrivial Z2 topological metal. Interestingly, the topologically protected Dirac point is visible at around the Fermi energy. This emergence originates from the inherent feature of the LaO with La 5d-4f orbital transition in energy driven by the strong octahedral crystal-field. The existence of novel surface states further unambiguously demonstrates the topological signature of LaO superconductor in its normal state.

Theoretical Calculations. — In the first-principles calculations [19–21], the plane wave basis method and the Perdew-Burke-Ernzerhof exchange correlation potential [22] have been used as implemented in the VASP code [23]. A 600 eV cutoff in the plane wave expansion and a 20 × 20 × 20 Monkhorst-Pack k-grid are chosen to ensure the calculations with an accuracy of 10−5 meV, and the lattice constants are optimized until forces on individual atoms are smaller than 10−3 eV/Å to obtain sufficient accuracy throughout the calculations. Furthermore, the spin-orbit coupling is also included in the theoretical calculations with the second variational method [24], and the phonon dispersion is calculated using the density functional perturbation theory within the phonopy code [25, 26].

Figure 1(a) shows the crystal structure of rare-earth binary oxide superconductor LaO, which crystallizes in a face-centered-cubic (fcc) structure of rock-salt type with space group Fm-3m. The optimized lattice constants of LaO are a = b = c = 5.158 Å, in good agreement with the previous experimental values (a = b = c = 5.144 Å) [27] and theoretical calculations (a = b = c = 5.164 Å) us-
ing an ultrasoft pseudopotential [18]. The corresponding BZ of the primitive cell of LaO along with the high-symmetry k-point is depicted in Fig. 1(b). The stability of the optimized lattice structure of LaO is also examined by the calculation of phonon spectrum, as shown in Fig. 1(c). There is an absence of the imaginary frequency in the phonon spectrum in Fig. 1(c), demonstrating the dynamical stability of the rock-salt structured lanthanum monoxide LaO.

The calculated electronic band structure of LaO is shown in Fig. 1(d). Clearly, there is a single-band passing through the Fermi level $E_f$ across the BZ, suggesting the metallic behavior of LaO superconductor in the normal state [also see the Fermi surface topology in Fig. S1 in supplementary materials (SM)]. This result is expected from our intuition that for the La$^{2+}$ ion in the monoxide LaO, the nominal number of the configuration La$^{2+}$: $5d^44f^0$ electron is 1, the lowest-lying conduction band is thus partially occupied. In the vicinity of the Fermi level $E_f$, it is interesting to point out that there is an intriguing Dirac point (0.2 eV above the $E_f$ with extra 0.2 $e^-$) appearing at the high symmetric W point in BZ [28, 29]. Although the appearance of Dirac point in three-dimensional systems with preserving both the time-reversal and inversion symmetries, where two Weyl points overlap in momentum space, is usually unstable, the crystal symmetry of $C_{4v}$ at W point in BZ will protect the stability of Dirac point in LaO (also see the strained band in Fig. S2 in SM) [20, 31]. In addition, we also notice that there is a band crossing feature above the $E_f$ in the energy of 0.96 eV, indicating the existence of band inversion in the electronic band structure of LaO.

These results strongly imply the electronic structure of LaO superconductor in the normal state to be a nontrivial topological metallic phase in three dimensions [29].

To quantitatively inspect the nontrivial topological phase of LaO, we further carry out the calculations of the $Z_2$ topological index since the time-reversal symmetry is invariant in LaO (see the magnetization calculations with magnetic configurations in Fig. S3 listed in Table S1 in SM) [32, 33]. In addition to the existence of the spatial inversion symmetry in rock-salt structured LaO, the calculation of the $Z_2$ topological invariant can be dramatically simplified by the so-called “parity method” [33, 38]. Accordingly, the $Z_2$ topological invariant of LaO can be obtained from the wavefunction parities $\delta_i^k$ at the Fermi level $E_f$ at the eight time-reversal invariant k points defined as $\Gamma_i = (n_1a^* + n_2b^* + n_3c^*)$, where $a^*$, $b^*$, and $c^*$ are primitive reciprocal lattice vectors shown in Fig. 1(b) with $n_i = 0$ or 1, and determined by the quantities $\delta_i^k = \langle \Phi_{2k',\Gamma_i}|P|\Phi_{2k',\Gamma_i}\rangle = \pm 1$, which is actually the eigenvalue of parity operator $P$, and corresponds to even (odd) parity of the Bloch functions $\{|\Phi_{2k',\Gamma_i}\rangle\}$ at the $2k'$-th band and the time-reversal invariant k point $\Gamma_i$. Here, it should be noting that we use the band numbering scheme from the calculations of density functional theory because LaO is a metal with no clear division between conduction and valence states shown in Fig. 1(d) [37, 39]. For an fcc lattice of LaO, we have the following eight time-reversal invariant k points: one $\Gamma = (0,0,0)$, three $X = (\frac{1}{2},\frac{1}{2},0)2\pi/a$, and four $L = (\frac{1}{2},\frac{1}{2},\frac{1}{2})2\pi/a$, shown in Fig. 1(b). The calculated parities on LaO at these time-reversal invariant k points with a given band index $\kappa(= 2k')$ around the Fermi level $E_f$ shown in Fig. 1(d) (Kramers degenerate bands, $\delta_i^k = \delta_i^{2k'-1}$) are listed in Table I. The $Z_2$ topological invariants $(\nu_0; \nu_1\nu_2\nu_3)$ between each pair of bands (k) near Fermi level $E_f$ in three dimensions are thus evaluated through the product of the parities $\delta_i^k$ at the time-reversal invariant k points, defined as $(-1)^{\nu_0} = \Pi_{i=1}^{8}\delta_i^k$ and $(-1)^{\nu_k} = \prod_{n_k=1,n_{j\neq k}=0,1,2}^{8}\delta_i^{n_k} = (n_1n_2n_3)$, where $\nu_0$ is the

| Band | $3 \times \delta_i^k$ | $4 \times \delta_i^k$ | $Z_2$ |
|------|----------------|----------------| ------|
| Band 24 | -1 | -1 | +1 | (0:000) |
| Band 22 | +1 | -1 | -1 | (1:000) |
| Band 20 | +1 | -1 | -1 | (1:000) |
| Band 18 | +1 | +1 | -1 | (0:000) |

TABLE I. Parities $\delta_i^k$ at the $k$-th band and the eight time-reversal invariant k points [one $\Gamma = (0,0,0)$, three $X = (\frac{1}{2},\frac{1}{2},0)2\pi/a$, and four $L = (\frac{1}{2},\frac{1}{2},\frac{1}{2})2\pi/a$] for LaO. Due to the Kramers degeneracy, we only list the parities on the even numbers bands. The nontrivial $Z_2$ topological invariants are evaluated through the product of the parities $\delta_i^k$ at the eight time-reversal invariant k points on a selected band with index of $k$ corresponding to that shown in Fig. 1(d).
strong topological index and is independent of the choice of primitive reciprocal lattice vectors $\Gamma_{j}$, while $\nu_{1}$, $\nu_{2}$, and $\nu_{3}$, denoted as weak topological indexes, are not. Interestingly, the existence of nonzero topological index listed in Table I allows the identification of the normal state of $Z$ in Table I, which is responsible for the intra-atomic transition in energy from outer shell 5$f$ to inner shell 4$f$ orbitals accompanying with the parity-switching (see Fig. [2]). For the La$^{2+}$ ion, the nominal number of conducting electrons is 1, and partially occupies the lowest-lying conducting band. Here it should be pointing out that the spin-orbit coupling has been neglected in the discussions on the orbital splitting shown in Fig. [2] because LaO is a single-band metal shown in Fig. [1(d) and the spin-orbit coupling will be significantly quenched. We also examine the electronic band structure without inclusion of spin-orbit coupling and find that the electronic dispersion near the Fermi level remains qualitatively unaltered (see Fig. S5 in SM). This orbital splitting picture is similar in sense to that in the topological Kondo insulating state in SmB$_{6}$ and YbB$_{12}$ [4, 41, 42]. Therefore, the strong octahedral crystal-field splitting drives the intra-atomic transition from 5$d$ to 4$f$ orbitals of La, leading the lanthanum monoxide superconductor LaO to be a nontrivial $Z_{2}$ topological metal in its normal state.

The density of states (DOS) are also carried out for the quantitative calculations to gain more insight into the aforementioned orbital splitting picture shown in Fig. [2]. In Fig. [3(a)], we find that the electronic states around the Fermi level $E_{f}$ are mainly originated from the conduction 5$d$ orbitals hybridized strongly with La 5$f$ orbitals (also see Fig. [2]). Considering that the charge distribution of lower-lying orbitals $t_{2g}$ do not directly point to the oxygen anions in octahedral crystal-field, and their interaction is relatively stronger than that for $a_{2u}$ orbital, and hence the $t_{2g}$ levels will lie much lower in energy than $a_{2u}$. As a result, the system undergoes an orbital transition between $t_{2g}$ of 5$d$ and $a_{2u}$ of 4$f$ orbitals accompanying with the parity-switching (see Fig. [2]). For the La$^{2+}$ ion, the nominal number of conducting electrons is 1, and partially occupies the lowest-lying conducting band. Here it should be pointing out that the spin-orbit coupling has been neglected in the discussions on the orbital splitting shown in Fig. [2] because LaO is a single-band metal shown in Fig. [1(d) and the spin-orbit coupling will be significantly quenched. We also examine the electronic band structure without inclusion of spin-orbit coupling and find that the electronic dispersion near the Fermi level remains qualitatively unaltered (see Fig. S5 in SM). This orbital splitting picture is similar in sense to that in the topological Kondo insulating state in SmB$_{6}$ and YbB$_{12}$ [4, 41, 42]. Therefore, the strong octahedral crystal-field splitting drives the intra-atomic transition from 5$d$ to 4$f$ orbitals of La, leading the lanthanum monoxide superconductor LaO to be a nontrivial $Z_{2}$ topological metal in its normal state.

The density of states (DOS) are also carried out for the quantitative calculations to gain more insight into the aforementioned orbital splitting picture shown in Fig. [2]. In Fig. [3(a)], we find that the electronic states around the Fermi level $E_{f}$ are mainly originated from the contribution of La 5$d$ orbitals hybridized strongly with La 4$f$ orbitals. This result is consistent with the nature of electron configuration of 5$d^{1}4$f$^{0}$ of the La$^{2+}$ ion in the monoxide LaO, and is responsible for the intra-atomic transition in energy from outer shell 5$d$ to inner shell 4$f$ orbitals of La. Additionally, it is important to point out...
that there is an existence of the van Hove singularity in the vicinity of the Fermi level $E_f$ with its DOS of 0.7 states per eV per La atom, which will induce an effective reduction of the local electron Coulomb interaction, thereby enhancing the role of non-local electron correlations for the driving force of the appearance of superconductivity \cite{13}. Inspecting the orbital resolved DOS on La 5$d$ and 4$f$ orbitals shown in Fig. 3(b), the La 4$f$ orbitals mainly locate inside the octahedral splitting gap $\Delta_0 \approx 2.5$ eV between the upper-lying $e_g$ and lower-lying $t_{2g}$ orbitals split from the La 5$d$ orbitals, consistent with the orbital splitting picture schematically illustrated in Fig. 2 that the octahedral crystal-field splitting gap for 5$d$ orbitals is significantly larger than 4$f$ ones. At around the Fermi level $E_f$, we also notice that the $t_{2g}$ orbitals play a dominant role, followed by the $e_g$ orbital, corresponding to the trivial and nontrivial strong topological bands listed in Table I based on the orbital resolved electronic structure calculations, indicative of the $e_g$ orbital across the lower-lying $t_{2g}$ orbitals resulting in the appearance of topologically protected Dirac point (see the orbital resolved band in Fig. S6 in SM).

At last, we turn to discuss the topological surface states based on the idea of the bulk-edge correspondence of the $Z_2$ topological metal \cite{14, 15}. In order to reveal the topological features of the binary lanthanum monoxide LaO, we calculate the topological surface states of a semi-infinite system based on the surface Green’s function \cite{16, 17} constructed by the maximally localized Wannier function fitting to the first-principles band structure calculations \cite{18, 19}. The calculated dispersion of the surface states projected on the (001) plane, as shown in Fig. 3, is obtained by evaluating the imaginary part of the surface Green’s function \cite{20, 50}. As compared with the bulk band structure along [001] direction shown in Fig. S7 in SM, the Dirac-like topological states are clearly visible at $M$ point slightly above the Fermi level $E_f$ shown in Fig. 3, which is actually projected from $W$ point shown in Fig. 1(d) in the unfolding BZ. At around the center of BZ ($\Gamma$ point), additional surface states are also emerged as indicated by bright spots, which stem from the nature of inverted band shown in Fig. 1(d) associated with nonzero $Z_2$ number listed in Table I. These surface state results further reveal the nontrivial topological electronic band structure of superconducting LaO in its normal state, and could be directly detected by angle-resolved photoemission spectroscopy (ARPES) in experiments.

**Discussion**.—The intriguing $Z_2$ nontrivial topological band structure of superconducting LaO may be of great interest for stabilizing the formation of prominent Majorana modes within the vortex cores of a natively superconducting surface state that are important for fault-tolerant quantum computing \cite{51, 53}. Materials hosting both topologically nontrivial surface states and a native superconducting ground state are uncommon, with relatively few promising candidates identified in FeSe$_{1-x}$Te$_x$ \cite{54, 55} and recently discovered Kagome superconductor CsV$_3$Sb$_5$ \cite{57, 58}. Additionally, it is worthy pointing out that although the topologically protected Dirac point is slightly located above the Fermi level, the LaO system could be driven into such region with relatively light electron doping (about 0.2 e$^-$ shown in Fig. 1(d)), such as by changing the amount of oxygen vacancies in LaO thin film during the thin film deposition, which could also effectively tune the $T_c$ of its superconductivity \cite{14}. On the other hand, since the Dirac point emerged at around Fermi level $E_f$ in LaO shown in Fig. 1(d) is usually unstable in three-dimensional systems, the stable and topological protected Weyl points could be easily evolved from Dirac point by breaking of either time-reversal or inversion symmetries \cite{28, 29}. Therefore, we also suggest that the appealing Weyl superconductor could be realized in a candidate of LaO superconductor capped by EuO ferromagnetic insulator using the proximity effect of ferromagnetism to lift the time-reversal symmetry or by isovalent substitution of sulfur to break the inversion symmetry \cite{59}, which could be experimentally verified by in situ ARPES in future.

**Conclusion**.—Throughout the first-principles calculations on the newly discovered lanthanum monoxide superconductor LaO, we find that the strong electron correlation between 4$f$ and 5$d$ orbitals in La leads to the emergence of nontrivial topological band structure in its normal state, such as the existence of intriguing topologically protected Dirac point at around the Fermi energy and the appearance of topological signature of novel surface states. Our theoretical study provides crucial insights into the electronic structure of superconducting LaO, hereby laying down the basis for a solid understanding of the interplay of intriguing nontrivial topology and superconductivity.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4}
\caption{(color online) The surface states of LaO projected on the (001) plane. Warmer colors represent higher local DOS and blue regions indicate the bulk band gap. The Fermi energy is set to zero.}
\end{figure}
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