Doping-dependent Phase Diagram of LaOM\textit{M}As (\textit{M}=V–Cu) and Electron-type Superconductivity near Ferromagnetic Instability

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Abstract. - By first-principles calculations, we present a doping-dependent phase diagram of LaOM\textit{M}As (\textit{M}=V–Cu) family. It is characterized as antiferromagnetic semiconductor around LaOMnAs side and ferromagnetic metal around LaOCoAs. Both LaOFeAs and LaONiAs, where superconductivity were discovered, are located at the borderline of magnetic phases. Extensive Fermi surface analysis suggests that the observed superconductivity is of electron-type in its origin. We discuss possible pairing mechanisms in the context of competing ferromagnetic phases found in this work and the ferromagnetic spin fluctuations.

The studies on new superconductors, particularly non-cuprate layered compounds, are always exciting and open up new windows for the possible further raising of transition temperature $T_\text{c}$. Except few of non-transition-metal compounds, such as MgB\textsubscript{2}, where superconductivity with $T_\text{c}$ up to 39K was found [1], problems in many cases are as complicated and challenging as what we found in cuprates. In the layered ruthenates, the ferromagnetic spin fluctuation is important and spin-triplet $p$-wave character was suggested [2] for the superconductivity found in Sr\textsubscript{2}RuO\textsubscript{4} with $T_\text{c}$ ~1K [3]. In a more recent example Na\textsubscript{x}CoO\textsubscript{2}·(H\textsubscript{2}O)\textsubscript{y} [4], the geometry fluctuations due to triangle-lattice are extensively discussed [5]. Here we will show that a rich doping-dependent phase diagram can be realized in the new family of layered compounds LaOM\textsubscript{P} or LaOM\textsubscript{As} (\textit{M}=V–Cu), where up to $T_\text{c}=26$K superconductivity was reached very recently in LaOFeAs after F-doping [6–8].

The quaternary oxypnictides LaOM\textsubscript{As} crystallize in layered tetragonal structure with $P4/\text{mm}$ symmetry [9]. Each transition-metal (oxygen) layer is sandwiched by two nearest-neighbor As (La) atomic layers, which form edge-shared tetrahedrons around the $M$ (oxygen) sites. The (MAs)$^-$ and (LaO)$^+$ triple-layer-subgroups stack alternatively along the c-axis. The positions of La or As sheets are determined by two internal parameters, $z_{\text{La}}$ and $z_{\text{As}}$, which define the inter-layer distances of La-O and M-As, respectively. It is important that this series of compounds are chemically stable such that systematical tuning is available without altering the structure and symmetry significantly. For instance, a variety of compounds can be synthesized by the replacement of transition-metal elements, where both the electron doping and hole doping can be realized by replacing O\textsuperscript{2–} or La\textsuperscript{3+} ions. Except the early report for the structure study [9], the detailed studies on the electronic and magnetic properties for this series of compounds are still in its early stage. It was first reported in 2006 that superconductivity can be realized in LaOFeP below 4K, and the $T_\text{c}$ was increased to 7K by F-doping [6]. Later, superconductivity with $T_\text{c}$ about 2K was reported for LaONiP [7], and $T_\text{c}$ around 26K was reached very recently in LaOFeAs again after F-doping [8]. We will present in this letter that both $M=$Fe and Ni compounds locate at special positions of the global phase diagram for the series of $M$ substituted compounds. The competing magnetic and superconducting phases found in our global phase diagram provide important clues on the possible pairing mechanism in this class of materials.

The phase diagram is constructed from first-principles calculations based on density functional theory with generalized gradient approximation (GGA) of PBE-type [10] for the exchange-correlation potential. We use the plane-
wave pseudopotential method, and the ultra-soft pseudopotential scheme [11] is adopted. The convergence of total energy calculations with respect to number of K-points and cut-off energy (of plane wave expansion) is well checked, and final results are double checked using the full-potential linearized augmented plane-wave (FLAPW) method (WIN2K package) [12]. The series of LaOMAs compounds with \( M \) ranging from V to Cu are all studied with full lattice optimizations using experimental 2 Fe cell, and the non-magnetic (NM), ferromagnetic (FM), and (intra-layer) antiferromagnetic states are treated. The same approach has been also applied to LaOMP series, qualitatively same results are obtained, we therefore concentrate our following discussions on LaOMAs series for consistence. 

As shown in Table I, the optimized lattice parameters and internal coordinates for Fe and Ni compounds are in excellent agreement with available experimental data [6–9], which demonstrates the quality of our present calculations. The optimized parameters are used in our calculations for all the compounds. Moving from V to Cu, the lattice parameters are only slightly modified, despite of the dramatical change of number of 3d electrons (from \( d^3 \) of V\(^{2+} \) to \( d^9 \) of Cu\(^{2+} \)), suggesting the less sensitivity of lattice distortion. 

Fig.1 shows the phase diagram computed for the whole range of compounds. The solid lines and the dashed lines represent the stabilization energies of FM and AF states relative to NM solution, respectively. Two distinct phase regions can be identified: the dome below Fe gives AF states, while the magnetic moment of the ferromagnetic ground state, while the one around Co is ferromagnetic. The computed magnetic moments (see Fig.1) show that strong nesting effect exists particularly for LaOFeAs. This will lead to stripe-type spin-density-wave (SDW) ground state with \( \sqrt{2} \times \sqrt{2} \) super-cell structure. The detailed results for this SDW state will be presented in a separate paper combined with experimental results [13].

To understand the electronic structures, we show the total and projected density of states (DOS) of various compounds in Fig.2. Let’s start from LaOFeAs (Fig.2(a)). The states between -2eV and +2eV are mostly from Fe-3d states, just below which are the states of O-\( p \) and As-\( p \) (from -6eV to -2eV). The \( p-d \) hybridization between O and Fe is negligible, while that between As and Fe is sizable. This As-\( M \) \( p-d \) hybridization is enhanced by changing to Ni compound (see the projected DOS of Fig.2(b)). Since the transition metal sites are coordinates by As-tetrahedron, the crystal field will normally splits the five \( d \) orbitals into low-lying two-folds \( e_g \) states and up-lying three-folds \( t_{2g} \) states. However, the As-tetrahedron are actually much distorted from its normal shape (squeezed along \( c \) by about 20\%). This distortion will further split the \( e_g \) and \( t_{2g} \) manifolds significantly making the final orbital distributions complicated. As the results, what actually happens is opposite to what we expect from simple tetraedra crystal field: the low-lying manifold is three folds and the higher-lying manifold is two folds, between which a pseudo-gap about 0.5eV exists. For Fe compound, the nominal number of \( d \) electrons is 6, and the low-lying three-fold bands are nearly fully occupied with the Fermi level \( E_F \) located very close to the deep of the pseudo-gap. If the crystal field is strong enough, which may be achieved by the substitution of As atoms, a simple band-insulator will be expected by enlarging the pseudo-gap. From the calculated DOS at \( E_F \), we estimate the bare susceptibility and specific heat coefficient, which are \( \chi_0 = 7.6 \times 10^{-5} \text{emu/mol} \) and \( \gamma_0 = 5.5 \text{mJ/K}^2\text{mol} \) for Fe compound (see Table I for
other compound). Taking the experimental susceptibility about 50 × 10^{-5} emu/mol at 300K, a renormalization factor about 6.6 is suggested, which is close to that shown in Sr2RuO4 [14].

Moving to Mn compound, the half filled d-shell (about d^5) will gain energy from the Hund’s coupling, and the spin polarized states will be favored as the results. In reality, the calculated total energies of both FM and AF solutions are much lower than that of NM solution (about 0.3eV/f.u for the former and 0.55eV for the later). The reason why the AF solution is more favored is that a gap about 0.2eV is opened in the AF solution (see Fig.2(e)). It is mentioned (but without showing data) in the recent experimental paper [6] that LaOMnP is a semiconductor. This is consistent with our prediction, and further we show that the ground state of Mn compound is AF.

The calculated spin moment is about 3.1 \( \mu_B \). This is consistent with our prediction, and further we show that the ground state of Mn compound is AF. However, our calculated occupation numbers of projected 3d-shell orbitals are quite uniform, suggesting this possibility is unlikely. The second possibility is due to either p-d or d-d hybridization (particularly for narrow gap system). The calculated spin moment is about 4.3\( \mu_B \)/Mn for typical high-spin AF insulator MnO [15], where only the p-d hybridization is important. However, here we point out that the Mn-Mn distance in LaOMnAs is about 2.8 Å, which is much shorter than what was found in MnO (about 3.2 Å), and is actually very close to the distance in elementary-Mn (about 2.6-2.7 Å). The direct d-d hybridization will be much enhanced by such short distance, which will again reduce the moment. The effect of direct d-d overlap has been addressed in previous study for LaOFeP [16], however we emphasize here that this is generally true for all the compounds of this family as shown by the optimized structure (Table I).

The stabilization of FM phase region at the right hand side has different origin as will be discussed here for LaOCoAs. Co has one more d electron than Fe, therefore the Fermi level is lifted up and located above the pseudo-gap. What is interesting is that a strong Van-Hove singularity (VHS) is present just at the Fermi level of LaOCoAS NM DOS as shown in Fig.2(d). The high N(E_f) in the presence of this VHS will push the system to be itinerant FM due to Stoner instability. This mechanism is further supported by the following factors: (1) the FM region is relatively narrow; (2) the polarized spin moment is small (about 0.5\( \mu_B \)/Co); (3) the energy gain is also small (about 35meV/f.u.). By adding one more electron, for LaONiAs, the Fermi level is shifted away from the VHS, the system is recovered to be NM again as shown in the phase diagram.

Having finished the discussions for the phase diagram and the general picture of the electronic structure, now let us focus on the LaOFeAs and LaONiAs, where superconductivity are discovered. Fig.3 gives the calculated band structures and Fermi surfaces (FS) for both compounds (the window for d-bands is shown, and there are totally ten d bands in our unit cell). First of all, the band dispersions along the z direction are all very weak suggesting the 2-dimensional nature of those compounds. Considering the in-plane dispersions, the band structure of LaOFeAs can be schematically separated into two parts. The bands below \( E_f \) are relative flat and have little contribution coming from the As-p states, while the bands above \( E_f \) are quite dispersive (except some flat branches around +1eV which corresponds to the VHS discussed above), and have large weight coming from the As-p character (as shown by the projected fat-bands plot). Those dispersive bands form electron-like FS cylinders around the M-A lines of the Brillouin zone, and hole-like FS cylinders are formed around the Γ-Z lines due to the Fermi level crossing of the bands from the lower part. For LaONiAs, all the flat bands are pushed down to below Fermi level, and only the dispersive bands remain to cross the Fermi level, which give the large electron FS around M-A lines, but hole-type FS around X-R line instead of Γ-Z.

The experimental results show that the LaOFeAs is superconducting only after electron-type F-doping [8], and also the \( T_c \) of LaOFeP (which has very similar band struc-
A phase of $^3$He [18]. Our calculations shows that LaOFeAs can be basically characterized as low density electron carriers doped on top of a band insulator with filled $d^6$ valence orbitals. In $^3$He, the B phase is realized under the low or ambient pressure condition while A phase is realized under high pressure condition close to solidification. By analogy, we suggest that the low electron density system LaOFeAs is in the weak coupling limit, which generally favors the unitary, or B phase like, pairing symmetry. Upon further increasing doping, the non-unitary A phase could be realized. In two dimensions, unitary B state can be characterized as a state where the up (down) spin electrons are paired in the $p_x + ip_y$ ($p_x - ip_y$) state, so that the time reversal symmetry is preserved. This state is similar to the topologically non-trivial state, characterized by $Z_2$ invariant [19], found in quantized spin-Hall insulator [20]. In contrast, the time reversal symmetry breaking A phase could be realized in Sr$_2$RuO$_4$ partly because the carriers density is high.

The topological nature of the proposed pairing state for LaOFeAs implies the existence of counter-propagating edge states which can be tested experimentally. In the bulk, the pairing state is fully gapped, and STM experiment would show a full gap in the I-V characteristics. However, moving to the edge, the STM experiment would show a gapless spectrum, revealing the gapless edge states protected by the time reversal symmetry. Most strikingly, in the presence of a magnetic impurity near the edge, the local density of states would show a gap again, due to breaking of time reversal symmetry.

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Doping-dependent Phase Diagram of LaOMAs (M=V–Cu) and Electron-type Superconductivity near Ferromagnetic Instability

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