Phase diagram of the three-orbital Hubbard-Holstein model simulating Superconducting Tungsten Bronze $A_xWO_3$

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Abstract. The superconductivity in tungsten bronze $A_xWO_3$ ($A=$alkali metal) is studied based on first-principles calculations and orbital fluctuation theory. We discuss the effects of the electron-Jahn-Teller phonon interaction and the on-site Coulomb interaction in the random phase approximation, and obtain a phase diagram on the $U-g$ plane in the low-doped regime at $x\sim0.05$, where high-temperature superconductivity has been experimentally observed.

1. Introduction
Tungsten bronze $A_xWO_3$ ($A=$alkali metal) is known to exhibit superconductivity, and the superconducting transition temperature $T_c$ increases rapidly up to 7 K with decreasing $x$[1,2] and a remarkable high-$T_c$ superconductivity with $T_c=91$K is reported at further low doping $x\sim0.05$[3] and $T_c=120$ K for $A=H$ [4]. The system also exhibits a rich set of structural phases, which are well explained by ab initio calculations [6]. However, relation between $x$ and the superconducting transition temperature by first-principles calculations has not yet been clarified. In addition, the superconductivity near the structural phase transition implies strong ferro-orbital fluctuations, and the W-5$d$ electrons have strong Coulomb interactions, which may play a crucial role in determining $T_c$. The aim of this work is to study the superconductivity in $A_xWO_3$ based on the effects of ferro-orbital fluctuations and on-site Coulomb interaction in the random phase approximation (RPA).

2. Orbital-fluctuation effect
Non-doped WO$_3$ is a band insulator with a band gap of 3 eV, and the conduction band consists mainly of $t_{2g}$ three orbitals of W-5$d$ electrons. In the case of alkali-doped $A_xWO_3$, angle-resolved photoemission spectroscopy (ARPES) revealed that the Fermi level shifts to the conduction band, as realized by the rigid-band shift image, while the band dispersion hardly changes[5]. Then, the tight-binding model model consisting of $t_{2g}$ three orbitals was constructed to reproduce the conduction bands of WO$_3$ using WIEN2k and the maximally localized Wannier function, and this model was applied to $A_xWO_3$[7]. There is a significant degeneracy in the conduction band, but it is resolved by the Jahn-Teller distortion that causes the structural transition[6].

Next, we consider the electron-phonon interaction between the $t_{2g}$ electron, the Jahn-Teller phonon, and the Coulomb interaction given by the Hamiltonian below
respectively, and 

\[ H_{el-ph} = \sum_{i,s} \sum_{m,m'} \sum_{\sigma} g_s^{m,m'} c_{im\sigma}^\dagger \hat{c}_{im'\sigma} (\hat{b}_{is} + \hat{b}_{is}^\dagger), \]  

(1)

\[ H_{el-el} = \frac{1}{2} U \sum_i \sum_{m \neq \sigma} \sum_{\sigma'} c_{im\sigma}^\dagger \hat{c}_{im\sigma} \hat{c}_{im\sigma'}^\dagger \hat{c}_{im'\sigma'} \]

\[ + \frac{1}{2} U' \sum_i \sum_{m \neq \sigma} \sum_{\sigma'} c_{im\sigma}^\dagger \hat{c}_{im'\sigma} \hat{c}_{im'\sigma'}^\dagger \hat{c}_{im'\sigma'} \]

\[ + \frac{1}{2} J \sum_i \sum_{m \neq \sigma} \sum_{\sigma'} \hat{c}_{im\sigma}^\dagger \hat{c}_{im'\sigma} \hat{c}_{im'\sigma} \hat{c}_{im\sigma} \]

\[ + \frac{1}{2} J' \sum_i \sum_{m \neq \sigma} \sum_{\sigma'} \hat{c}_{im\sigma}^\dagger \hat{c}_{im\sigma} \hat{c}_{im'\sigma} \hat{c}_{im'\sigma} \]  

(2)

Here, \( c_{im\sigma}^\dagger \) is the creation operator for site \( i \), orbit \( m = d_{xy}(1), d_{yz}(2), d_{zx}(3) \), and spin \( \sigma \), and \( \hat{b}_{is}^\dagger \) is for site \( i \) and mode \( s \). In addition, \( U \) and \( U' \) are intra- and inter-orbital direct terms, respectively, and \( J \) and \( J' \) are Hund’s coupling and pair transfer, respectively. The Hamiltonian Eq. (1) was found to reproduce the doping dependence of the structural transitions within the adiabatic approximation, in agreement with experiment [5].

To discuss orbital fluctuations that are enhanced by electron-phonon interactions and diverge toward second-order structural transitions, the RPA method is employed for the electron-phonon interaction in Eq. (1) and the Coulomb interaction in Eq. (2). The RPA charge-orbital susceptibility \( \hat{\chi}^c(q) \) and spin susceptibility \( \hat{\chi}^s(q) \) are given by

\[ \hat{\chi}^c(q) = \hat{\chi}^0(q) \left[ 1 + \hat{\Gamma}^c(i\omega_n) \hat{\chi}^0(q) \right]^{-1}, \]

(3)

\[ \hat{\chi}^s(q) = \hat{\chi}^0(q) \left[ 1 + \hat{\Gamma}^s(i\omega_n) \hat{\chi}^0(q) \right]^{-1}, \]

(4)

where the bare susceptibility is defined as \( \hat{\chi}^0(q) = -\langle T/N \rangle \sum_k \hat{G}(k + q) \hat{G}(k) \rangle \). Here, \( k = (k, i\varepsilon_n) \) and \( q = (q, i\omega_m) \), and \( \varepsilon_n = (2n + 1)\pi T \) and \( \omega_m = 2m\pi T \) are the fermionic frequency and boson Matsubara frequency, respectively. In Eq. (3), \( \hat{\Gamma}^c \) represents the charge-orbital vertex and in Eq. (4), \( \hat{\Gamma}^s \) represents the spin vertex, which is given as

\[ \hat{\Gamma}^c(i\omega_m) = \hat{\Gamma}^{c(0)} - 2 \sum_s g_{s}^{m_2m_1} g_{s}^{m_3m_4} D_s(i\omega), \]

(5)

\[ \hat{\Gamma}^s(i\omega_m) = \hat{\Gamma}^{s(0)}, \]

(6)

\[ \hat{\Gamma}^{c(0)} = \begin{cases} \frac{U}{2} & (l_1l_2l_3l_4) = (llll) \\ -U' + \frac{2J}{2} & (l_1l_3l_4l_4) = (ll'l') \\ 2U' - J & (l_1l_2l_4l_4) = (ll'li') \\ J' & (l_1l_4l_2l_3) = (llll') \end{cases} \]

\[ \hat{\Gamma}^{s(0)} = \begin{cases} U' & \\ J' \end{cases} \]

(7)
where \( D_S(i\omega_m) = 2\omega_s / (\omega_m^2 + \omega_s^2) \) is the Green’s function of the local phonon for mode \( s \). Note that the charge-orbit instability occurs when the maximum eigenvalue \( \alpha_c \) of \( \Gamma^c(i\omega_m)\chi^c(q) \) at \( i\omega = 0 \) becomes 1. In this paper, we consider only the tetragonal mode with

\[
\frac{2}{\sqrt{3}} g_{\text{tetra}}^{11} = -\frac{1}{\sqrt{3}} g_{\text{tetra}}^{22} = -\frac{1}{\sqrt{3}} g_{\text{tetra}}^{33} = g,
\]

and set \( \omega_s = 0.02 \text{ eV} \) for simplicity.

We investigate superconductivity by solving the linearized Eliashberg equation, and find the eigenvalues \( \lambda \) proportional to the superconducting gap function \( \Delta \) and the eigenvector. The linearized Eliashberg equation is

\[
\lambda \Delta_{mm'}(k) = -\frac{T}{N} \sum_{k'} \sum_{m_i} V_{mm1,m2m'}(k-k')G_{m3m1}(-k')G_{m4m2}(k')\Delta_{m3m4}(k')
\]

where \( \hat{V}(q,\omega) \) is expressed by the following equation,

\[
\hat{V}(q) = \frac{3}{2} \hat{\Gamma}^s(i\omega_m) \hat{\chi}^s(q) \hat{\Gamma}^s(i\omega_m) - \frac{1}{2} \hat{\Gamma}^c(i\omega_m) \hat{\chi}^c(q) \hat{\Gamma}^c(i\omega_m) + \frac{1}{2}(\hat{\Gamma}^{(s,0)} - \hat{\Gamma}^{(c,0)})
\]

As \( T \) decreases, \( \lambda \) increases with increasing \( \alpha_c \) and finally becomes unity at \( T = T_c \). The corresponding gap function \( \Delta_{xy} \) is shown in Fig. 1. Even with the gradual addition of on-site Coulomb interaction \( U \), and the symmetry of the pair is anisotropic s-wave. Because Fig. 1 shows the \( d_{xy} \) orbital component at \( k_z = 0 \) has a large anisotropy, but this is due to the nature of the orbitals on the Fermi surface, and the on-site Coulomb interaction \( itU \) does not change. The \( d_{xy} \) orbital component of the susceptibility is found to be most dominant in the Jahn-Teller phonon. In this case, \( \Delta_{xy} \) is the main component of the order parameter.

The value of \( T_c \) obtained for \( x = 0.05 \) was found to be a significant improvement over the value from standard BCS theory. And it means that it has high \( T_c \) superconductivity in the low carrier region. Effects of the on-site coulomb interaction \( U \) and the Jahn-Teller electron-phonon coupling \( g \) are taken into account within the random phase approximation (RPA). We obtain the phase diagram on the \( U-g \) plane as shown in Fig. 2, where the instability towards the magnetic order is observed for a huge value of \( U \sim 28 \text{ eV} \) almost independent of \( g \) while the
instability towards the ferro-orbital order accompanied by the cubic-tetragonal structural phase transition is observed for a realistic value of $g=0.21\sim0.28$ eV depending on $U$. Superconductivity is investigated by solving the linearized Eliashberg equation for the pairing interaction obtained by RPA, and we find that $T_c$ for the anisotropic $s$-wave symmetry is largely enhanced due to the ferro-orbital fluctuation in the vicinity of the ferro-orbital order (structural phase transition) [7] as compared with that for the isotropic $s$-wave symmetry from the McMillan equation in which the $\chi$-dependence of the coulomb pseudopotential due to the plasmon effects is considered to reproduce the experimental $\chi$-dependence of $T_c$ up to 7K [8].

3. Conclusion
We have investigated the three-orbital Hubbard-Holstein model simulating superconducting tungsten bronze $A_x$WO$_3$ using the RPA and the linearized Eliashberg equation, and have found that the anisotropic $s$-wave superconductivity is mediated by the orbital fluctuation at $x=0.05$ for realistic values of parameters $g\sim0.28$ eV and $U\sim4$ eV and is expected to be realized in the low-doped $A_x$WO$_3$ which shows a high-$T_c$ superconductivity. To be more conclusive, we need further calculations including low temperature where the superconductivity is observed such as 90 K. Such calculations are under way and explicit results will be published in subsequent paper.

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