

# The Competition between the CDW and the Superconducting State in Valence Skip Compounds

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**Abstract.** In some superconductors the charge density wave (CDW) state is adjacent to the superconducting state in the phase diagram. This CDW phase can be collapsed either pressure or by chemical doping, depending on compound. Among them, in so-called valence skip compounds, a large charge fluctuation with the large electron-phonon interaction is expected. We performed a first-principle study and investigated how the CDW gap is collapsed for several valence-skip compounds, i.e.  $\text{SnX}_3$ ,  $\text{RbTlX}_3$  ( $X=\text{F,Cl,Br,I}$ ) and  $\text{CsTlI}_3$ . For all these compounds we found that the CDW gap is rather robust for the uniform volume change, and on the contrary, the magnitude of the CDW gap strongly depends on the position of the anion. We found that this CDW gap is already collapsed at ambient pressure in  $\text{SnBr}_3$ ,  $\text{SnI}_3$  and  $\text{CsTlI}_3$ .

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## 1 Introduction

Searching for high- $T_c$  superconductors (HTSCs) is not only a central issue of condensed matter physics, but also an important task for applications. Nowadays most of the HTSCs are so-called exotic ones, which means that the superconducting (SC) gap is highly anisotropic [1]. The most typical HTSCs are the cuprates. In cuprates, a repulsive electron-electron interaction is used as a pairing "glue", therefore anisotropy inevitably occurs in the SC gap function. This anisotropy is an obstacle for the applications. Moreover, most of HTSCs have layered structure, and their workability is not good. In this sense, isotropic HTSC is highly desirable. If we can use attractive interaction as a glue of SC pairing, the resulting SC gap will be isotropic. In fact it realizes in the conventional

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phonon-mediated SCs, but their  $T_c$  are usually low because of the low Debye temperature. One of a scenario which gives a direct attractive interaction is the valence-skip (VS) model [2]. This model starts from an experimental fact that some elements skip a specific valence. For example, Bi takes 3+ or 5+ valence state and usually does not take 4+ valence state (i.e. skips 4+ state). The microscopic reason of this is still not clear, but a simple explanation is that an ion favors closed shell. In case of Bi, the configuration of the outermost valence electron is s2 (fully occupied) in  $\text{Bi}^{3+}$  ion and s0 (empty) in  $\text{Bi}^{5+}$  ion. This means that s1 configuration is unstable. In other words, if one electron comes to this site (s1 state), it favors that another electron occupies the same site (s2 state). This is nothing but an attractive interaction. The importance of s1 state is also pointed out by Sleight [3]. What happens if we put an atom on a site where it has to take s1 configuration? In thallium-doped PbTe, doped Tl substitutes  $\text{Pb}^{2+}$  and takes  $\text{Tl}^{2+}$  (s1) valence state. This system shows superconductivity, and its  $T_c$  is quite higher than the  $T_c$  estimated from its carrier density [4]. This situation can be described by the charge Kondo model, and it explains the experimental result well [5, 6]. Another example is  $\text{BaBiO}_3$ , which is known as the mother compound of HTSC,  $(\text{Ba},\text{K})\text{BiO}_3$  [7] and  $\text{Ba}(\text{Pb},\text{Bi})\text{O}_3$  [8]. In  $\text{BaBiO}_3$  these s1 states ( $=\text{Bi}^{4+}$ ) are periodically arranged, spontaneous symmetry breaking occurs and a charge disproportionation from 2s1 to s2+s0 state takes place. These s2 and s0 states are ordered so as to lower the Madelung energy [9]. We call this state as charge ordered state or charge density wave (CDW) state. This situation can be described by an extended Hubbard model, and the CDW and the SC states are adjacent in the phase diagram [10]. In most cases at the same time, a displacement of the surrounding anions also appears. This experimental fact suggests that the electronic system and lattice system are strongly coupled. In this case the CDW and the SC states are also adjacent in the phase diagram, naturally explains the phase diagram of  $\text{Ba}(\text{Pb},\text{Bi})\text{O}_3$  [11]. In any case, HTSC occurs at the vicinity of insulating CDW phase. In order to seek more HTSC compounds without anisotropy, it may be useful to explore more VS compounds. Recently it was reported that a large class of perovskite  $\text{ATiX}_3$  ( $\text{A}=\text{Rb},\text{Cs}$ ;  $\text{X}=\text{F},\text{Cl},\text{Br}$ ) show a electronic feature similar to  $\text{BaBiO}_3$  [12]. In these compounds Ti has 2+ (s1) state on average, and disproportionates to  $\text{Ti}^{1+}$  (s0) and  $\text{Ti}^{3+}$  (s2) state. These s2 and s0 states order like NaCl crystal, similar to the case of  $\text{BaBiO}_3$ . In general, there are two ways to melt this CDW and make the system metallic. One is carrier doping and the other is adding pressure. First-principles calculation shows that hole doped system  $\text{A}_{1-x}\text{TiX}_3$  is metallic and has the similar electronic structure as  $(\text{Ba},\text{K})\text{BiO}_3$ . Considering its electronic structure is similar to HTSC  $(\text{Ba},\text{K})\text{BiO}_3$ ,  $\text{A}_{1-x}\text{TiX}_3$  is also a good candidate of HTSC. Another way to melt the CDW order is adding pressure.

In the preceding paper we investigated the electronic structure of  $\text{RbTiX}_3$  ( $\text{X}=\text{F}, \text{Cl}, \text{Br}$ ) and found that the CDW gap at ambient pressure decreases as the size of anion increases. Moreover, we have revealed that  $\text{RbTiCl}_3$  and  $\text{RbTiBr}_3$  can be metallic with adding tractable pressure [13, 14]. A natural expectation is that if X is I then the CDW gap may further decrease and the system possibly becomes metallic at ambient pressure. Unfortunately  $\text{RbTiI}_3$  itself is not found in literature, maybe because A-site ion is too