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Electronic states of valence-skipping compounds

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Abstract. “Valence skip” means that an element leaps a particular valence state in compounds. For example, Bi forms the compounds in +3 and +5 valence states, and Tl forms in +1 and +3 valence states. In BaBiO₃, the average valence of Bi is +4, but the system spontaneously breaks its crystal symmetry and forms the charge density wave (CDW) state like (Bi³⁺,Bi⁵⁺). This means that the effective electron-electron interaction is attractive, contrary to the well-known on-site Coulomb repulsive interaction. In the valence skip compounds, it is expected that some carrier doping can induce superconductivity with high-T_c. For example, (Ba,K)BiO₃ shows high-T_c that is not plausible merely from the convectional electron-phonon mechanism. Tl-doped PbTe is also considered as the superconducting compound that Tl valence fluctuates and enhances T_c. We estimated the formation energy of the CDW in BaBiO₃, TlS and TlSe by evaluating the Madelung energy, in order to show the CDW state is more stable than the uniform charge state, and the valence skip is actually realized.

1. Introduction

Some elements have several ionic valence states, and in some cases they skip a particular valence. For example, Bi atom takes Bi⁴⁺ and Bi⁵⁺ but there is no Bi³⁺ ionic state, and Tl takes Tl¹⁺ and Tl³⁺ but there is no Tl²⁺ state. These elements are called as “valence skippers”. If Bi atoms are forced to take Bi⁴⁺ valence state on average in a compound, they spontaneously dissipate to Bi³⁺ and Bi⁵⁺. This means that the Coulomb interaction $U = E(3+) + E(5+) - 2E(4+)$ is negative, where $E(n⁺)$ is the energy of the Biⁿ⁺ state. This situation naturally leads to negative U Anderson or Hubbard model, and if the outermost orbital of this ion is the s-orbital, the ground state becomes diamagnetic (no Curie term)[1]. Negative-U impurity can induce superconducting pairing interaction[1-3]. Superconductivity found in (Ba,K)BiO₃[4] and slightly Tl-doped PbTe[5,6] are newly enlightened from this point of view[1,7-10]. On the other hand, if these valence-skip atoms are ordered in crystal and there are no extra carriers, the system will form a charge-density wave (CDW) state. This order is not determined only by its on-site interaction, but the intersite interactions are necessary. If we consider the two degrees of freedom (namely Bi³⁺ and Bi⁵⁺ ) as an isospin, when the intersite interaction is “antiferromagnetic”, these isopins will order as the “Néel order”. Thus we have to examine not only the on-site interaction $U$, but also the intersite interactions.

We pay attention to three insulating valence-skip compounds, BaBiO₃, TlS and TlSe. All of these compounds include valence-skip elements, namely Bi and Tl, and they are closely related to the superconducting compounds. BaBiO₃ is the parent material of Ba(Pb,Bi)O₃ and (Ba,K)BiO₃, and it is neither a band insulator nor a Mott insulator[1]. A band calculation based on the local-density
approximation shows that BaBiO$_3$ does not have a band gap, even though the crystal distortion found in neutron diffraction experiment is fully included[11]. Neutron diffraction experiments show that BaBiO$_3$ forms a charge-density wave (CDW)[12,13]. TlS and TlSe are also insulating, and they also form CDWs[14]. (Pb,Tl)Te is an exotic superconductor[7,10], and its Tc is almost proportional to the Tl content $\delta$, and it does not saturate until the solution limit $\delta_0$~1.5%. Thus we naturally expect that more inclusion of Tl can enhance Tc. If the Tl doping concentration reaches to 100% it becomes hypothetical TlTe. TlTe does not exist in nature, but isovalent TIS and TlSe exist. Therefore, TIS and TlSe are the hopeful candidates for superconductivity with valence-skip fluctuations.

In this paper we examine how the CDW state realizes in the valence skip compounds BaBiO$_3$, TlS and TlSe. We briefly introduce our method in Section 2, and in Section 3 we discuss how can the effective electron-electron interaction be negative, and how is the CDW state formed.

2. Methods

The first explanation of the negative-U behavior in BaBiO$_3$ is performed by Varma[1].

$$U^{4+}=E_5+E_3-2E_4$$

(1)

where $E_n$ is the total energy of the atom in the $n$th charged state. Here we obtain $U^{4+}=10.7$eV. This value is quite smaller than $U^{3+}=19.7$eV and $U^{5+}=32.3$eV, but is still positive.

For elucidating the negative-U behavior and the CDW order, we explicitly take the long-range Coulomb interaction into account. Since we only consider the insulating states, we restrict ourselves in an ionic model.

As a natural extension of the equation (1), we propose the following formula[9]

$$\Delta E = E_{Mad}(Ba^{2+}Bi^{3+}Bi^{5+}O^{2-}_6) - E_{Mad}(Ba^{2+}Bi^{4+}Bi^{4+}O^{2-}_6) + U^{4+}$$

(2)

here the first term and the second term denote the electrostatic (Madelung) energy for the uniform charge state (A) and CDW state (B) per primitive unit cell, respectively. When $\Delta E <0$, CDW state should be stabilized.

As for BaBiO$_3$, we neglect the small tilting of BiO$_6$ octahedra for simplicity. Then the crystal structure becomes the double perovskite type and its space group is O$_h$-Fm3m. In this simplified structure, the only atomic parameter which cannot determine only by symmetry is oxygen ($x$,0,0). Two types of Bi, hereafter we call them as Bi(1) and Bi(2), are alternatively ordered. If $x=0.25$, the oxygen atom is at the center of Bi(1) and Bi(2). When $x$ is larger than 0.25, the oxygen atom is moved toward Bi(2). Neutron diffraction experiments shows that $x$~0.26, when we neglect the small tilting of BiO$_6$ octahedra[12,13]. We set this $x$ as a parameter, calculate the Madelung energy for the charge states (A) and (B). Some details of the calculation are described in Ref.9.

Similarly for TlS and TlSe, experimentally found space group is D$_{4h}$-I4/mcm. This structure can be derived from the CsCl structure. There are two Tl sites similar to the two Bi site in BaBiO$_3$, but the order of Tl(1)-Tl(2) is so-called C-type, i.e. antiferro order in $a$-$b$ plane and ferro order along $c$-axis. Sulfur atoms are in 8h Wycoff position. The only one atomic parameter $x$ represents the displacement of the sulfur atom. Since the unit cell includes four Tl and four X atoms in TlX, then the equation (2) becomes

$$\Delta E = E_{Mad}(Tl^{1+}_1 \ Tl^{3+}_2 S^{2-}_4) - E_{Mad}(Tl^{2+}_1 \ Tl^{2+}_2 S^{2-}_4) + 2U^{2+}$$

(3)

here the first term and the second term denote the electrostatic (Madelung) energy for the uniform charge state (A) and CDW state (B), respectively. The third term corresponds to the ionic Coulomb interaction for Tl$^{2+}$ state, $U^{2+}$=9.4eV.
3. Results

3.1. BaBiO$_3$

Figure 1 shows the Madelung energy of BaBiO$_3$ for various charge states. We can find that at $x=0.282$ the charge-ordered (B) state becomes the ground state because the Madelung energy gain overcomes the loss of the ionic energy $U^{4+}$. The Madelung energy of (B) state is lower than (A) state even at $x=0.25$, but the displacements of oxygen atoms are necessary to form CDW. This value $x=0.282$ is rather larger than the value $x\sim 0.26$ which is determined by neutron diffraction experiments, but we consider that large polarizability of oxygen atom can reconcile this difference [9].

![Figure 1. Madelung energy of BaBiO$_3$.](image1)

![Figure 2. Madelung energy of TlSe.](image2)

3.2. TlS and TlSe

Figure 2 shows the Madelung energy of TlSe for the charge states mentioned above. This curve is almost similar to that of TlS[15], because we have used the same ionic charges. The small differences come from the different lattice constants. In fact, it is experimentally found that TIS and TlSe has almost the same atomic parameter $x$ (0.1721 for TIS and 0.18 for TlSe)[14,16]. Our calculation shows that CDW is stable below $x=0.11$ both for TIS and TlSe. The agreement between experiment and calculation is not good, compared to BaBiO$_3$. There are mainly two reasons: First, we only consider the displacements of anions which does not change the crystalline space group symmetry. The displacement vector of a sulfur atom $(x,x,0)$ does not direct to the Tl(2)-X (X=S,Se) bond, contrary to the case of BaBiO$_3$. Thus the change of $x$ does not lower the Madelung energy effectively. Second, we have ignored the covalent-bond effect. An X-ray diffraction experiment indicates that TIS has ionic-covalent bonds[16]. Tl$^{3+}$ has two empty 6s orbitals, then there is an energy gain by making chemical bond with the neighboring anions, and this energy gain increases when the bond-length decreases. Tetragonal coordination of the Tl(2) site also suggests the existence of sp$^3$ hybridized orbital. Since Se-4p orbitals are more expanded than S-3p orbitals, TlSe has more covalency than TIS. Therefore, the discrepancy between this calculation and the experiment may be larger in TlSe. As for BaBiO$_3$, since the deviation of $x$ from 0.25 is small, this effect only plays a secondary role[9].

TIS and TlSe both have the high-pressure phase. TIS and TlSe change their structure to cubic CsCl structure above 25GPa and 21GPa, respectively[16]. CsCl structure corresponds to the case $x=0.25$ with changing the c/a ratio. In this case TIS and TlSe should take the uniform charge state (A), and the experiment also suggests that the valence of Tl is 2+ [14]. The equilibrium position of anions themselves cannot be determined by this calculation, because they are determined by the balance between the attractive electrostatic interaction and the short-range ion-ion repulsive interaction.
Nevertheless, we can compare the electrostatic energies between (A) and (B) states for a particular position of anions, because the cohesive energy is almost determined by the electrostatic energy[17]. We expect that the valence-skip fluctuation will be very large in vicinity of the structural phase transition at 25/21GPa in TlS/Se.

Finally we discuss the condition that the valence skip fluctuation takes place. For simplicity we consider an impurity s-level which has the orbital energy $\varepsilon_s$ and effective Coulomb interaction $U(<0)$. When we define $E(n)$ as the energy which has $n$ electrons on this site, valence-skip fluctuation may be maximum when $E(0)=0$ and $E(2)=2\varepsilon_s+U$ have the same energy. This leads to a constraint: $\varepsilon_s=-U (=|U|)$. Possibly this is a reason why the compounds M:ZX (M:In,Tl,…; Z:Ge,Sn,Pb; X:S,Se,Te) do not show superconductivity except for Tl:PbTe[5]. Nevertheless, this mechanism of superconductivity is fascinating because it directly uses the electron-electron attractive interaction. Moreover, this type of interaction will give rise to new fruitful physics, such as charge-Kondo effect, superconductivity, and possible reentrance of normal state in extremely low temperature[7].

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