Evolution of the CDW gap in Valence Skipper RbTlX₃ (X=F,Cl,Br): A first-principle study

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Abstract. In the present study we investigated the electronic structure of the valence skipping compound RbTlX₃ (X=F,Cl,Br) from first principles. Combined with structural optimization, we confirmed that the charge-density-wave (CDW) is formed in all of these three compounds, and the Tl atoms in two different sites take the valence Tl¹⁺ and Tl³⁺. We investigated the evolution of the CDW gap as a function of the volume and the atomic position, and found that this CDW gap can be collapsed by applying pressure with only few GPa for RbTlBr₃. In this metallic phase a large charge-fluctuation and a large electron-phonon interaction is expected.

1. Introduction

BaBiO₃, which is the parent compound of the high-\(T_c\) superconductor (Ba,K)BiO₃, is a so-called valence skipper[1]. Since the formal valence of Bi in BaBiO₃ is the unstable 4⁺ state, Bi atoms spontaneously disproportionate to Bi³⁺ and Bi⁵⁺, accompanied with the displacement of anions[2]. These Bi³⁺ and Bi⁵⁺ ions are ordered like NaCl, and this charge order is also known as a charge density wave (CDW). Crystal symmetry is also lowered in this CDW phase. The hole doping in BaBiO₃ restores the high crystal symmetry, collapses the CDW gap, and induces high \(T_c\) superconductivity[3].

Since the valence skip ion can be an attractive center of conduction electrons, the induced superconductivity can be an isotropic one. This property is advantageous not only for high \(T_c\), but also for various applications. Therefore it is highly desirable to find other superconductors induced by valence skip fluctuation.

Recently such a kind of candidate compound is proposed by Schoop et al.[4]. They investigated the electronic structure of ATlX₃ (A=Rb,Cs; X=F,Cl,Br) and found that the electronic structure of ATlX₃ and BaBiO₃ quite resemble each other. They also predicted that carrier doping can melt the CDW order in RbTlCl₃, and the resulting metallic state is possibly superconducting.

In general, insulator can be metallic by carrier doping or pressure. In the present study we focus on the pressure effect. We found that RbTlCl₃ and RbTlBr₃ are very compressible, and a tractable (~several GPa) pressure may induce metal-insulator transition.

2. Details of Calculation
We have calculated the electronic structure of RbTlX₃ (X=F,Cl,Br) from first-principles. As for the crystal structure, we assume ordered perovskite structure which is seen in CsTlCl₃[5]: Space group #225 Fm-3m; Rb(1/4,1/4,1/4), Tl1(0,0,0), Tl2(0,0,1/2), X(0,0,z). This structure is essentially the same with that of BaBiO₃. Since the energy gap and the total energy are mainly determined by the breathing motion[4], we ignore tilting mode and concentrate on breathing mode. In this structure, the only one free structural parameters is the internal parameter z(X). Moreover, the lattice constant a, or the same thing, the unit cell volume V (=a³/4) is also a changeable parameter. These two parameters z(X) and V determine the whole electronic structure, including the total energy and the CDW gap Δ. We first set V by hand, and optimized z(X) for each V.

We have used a full-potential augmented plane wave (FLAPW) method within the general gradient approximation (GGA)[6]. The computer program package WIEN2k[7] was used in this work. The parameter RKₘₐₓ is chosen as 7.0. We took ~1000 k-point mesh in the first Brillouin zone for the self-consistent calculations.

3. Results and Discussions

Figure 1 shows the energy dispersion curves of RbTlX₃ (X=F,Cl,Br) for the optimized V (i.e. ambient pressure) and z(X). The optimized value of z(X) is 0.2246, 0.2362, 0.2371 for X=F,Cl,Br, respectively. We can see that a band gap opens between the LUMO mainly consisting of Tl₁-s state and the HOMO mainly consisting of Tl₂-s state. Since LUMO is empty and HOMO is fully occupied, Tl₁ atom becomes Tl³⁺ and Tl₂ atom becomes Tl¹⁺. This is consistent with the simple ionic picture that Tl₁-X distance should be shorter than Tl₂-X distance. The band gap Δ is an indirect one for all these three compounds, and the magnitude of Δ is 2.25eV, 0.74eV, 0.39eV for X=F, Cl, Br, respectively. As the size of anion increases, the hybridization between Tl-s and X-p orbitals increases, and z(X) approaches 0.25 (center of the two Tl atoms) and eventually Δ decreases. This kind of gap structure is also seen in some valence skippers, for example, SnF₃ and BaBiO₃[8].

Figure 1 Energy dispersion curves of RbTlX₃ (X=F,Cl,Br). The units of vertical axis are eV. The thickness of curves denotes the contribution of Tl₁-s orbital.
Since the magnitude of the CDW gap is quite small in RbTlCl$_3$ and RbTlBr$_3$, it is expected that external pressure can collapse this gap. We changed the lattice volume, and calculated the magnitude of the CDW gap. We also calculated the pressure at each volume by fitting the energy-volume plot to the Murnaghan equation of state.

Figure 2 shows the CDW gap of RbTlBr$_3$ with changing lattice volume. The dotted line shows $\Delta$ when $z$ is fixed to $z_0=0.2371$, which is the $z$ value at ambient pressure. In this case, $\Delta$ hardly changes with decreasing volume (or increasing pressure). However in fact, $z$ is a function of $V$, i.e. $z$ decreases with decreasing volume. And $\Delta$ is rather sensitive to the change of $z$, eventually $\Delta$ rapidly decreases and reaches zero when $V$ decreases $\sim$8 percent from the volume at ambient pressure. This is shown in the solid line of figure 2. Similarly, the CDW gap of RbTlCl$_3$ collapses at $\sim$13% volume reduction. The point that the CDW gap becomes zero is called a quantum critical point (QCP), which is a central interest in condensed matter physics. We can see that this pressure induced metal-insulator phase transition in RbTlCl$_3$ and RbTlBr$_3$ is a second-order one.

Figure 2 The CDW gap of RbTlBr$_3$ as a function of volume reduction ($\Delta V$). $\Delta V=0$ denotes the volume at the ambient pressure. The dotted line is for fixed $z=z_0$, and the solid line is for optimized $z$ for each $V$. For example, at the QCP ($\Delta V=8\%$) $z$ becomes 0.2412.

Figure 3 is the energy-volume plot of RbTlBr$_3$ fitted with the Murnaghan equation of state. Similarly to figure 2, the dotted line is fixing $z=z_0$ and the solid line is optimizing $z$ for each $V$. The solid line is always below the dotted line as expected. The obtained bulk modulus of RbTlCl$_3$ and RbTlBr$_3$ is 28GPa and 18GPa, respectively. These values are much smaller than that of BaBiO$_3$, i.e. 157GPa which is estimated by the high-pressure X-ray diffraction experiment[9].

The lower panel of figure 3 shows the pressure $P=dE/dV$. Combined with the result of figure 2, we can obtain the pressure at which the CDW gap closes. Since the bulk modulus is very small, the pressure at the QCP is $\sim$3.0GPa and $\sim$1.4GPa for RbTlCl$_3$ and RbTlBr$_3$, respectively. Considering the general tendency that GGA overestimates the itineracy, this pressure may become larger. Nevertheless, we predict that applying pressure with several GPa can collapse the CDW gap of RbTlBr$_3$. 
Figure 3 Upper panel: energy-volume plot of RbTlBr$_3$ fitted with Murnaghan equation of state. The dotted line is for fixed $z=z_0$, and the solid line is for optimized $z$ for each $V$. Lower panel: Pressure at each volume calculated by $P=dE/dV$ for the fitted $E(V)$. The vertical broken line denotes the volume at QCP.

Although the band structure of RbTlBr$_3$ is similar to BaBiO$_3$, BaBiO$_3$ does not show such a pressure-induced metal-insulator transition because of its large bulk modulus. Another example is InTe, which shows CDW at ambient pressure and superconductivity at very high pressure (37GPa)[10]. RbTlBr$_3$ may be the first case to show metal-insulator transition induced by a tractable pressure in the valence-skip compound.

We thank to H. Eisaki and K. Odagiri for useful discussions. This work was partially supported by KAKENHI (Grant No. JP26400379) from Japan Society for the Promotion of Science (JSPS).

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