Electronic structure of superionic conductors

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Abstract

In this review, the electronic structures of superionic conductors are summed up. Many studies on the electron state have been performed intensively in noble metal halides and noble metal chalcogenides. In the 1st section, the electronic state studies of AgI type superionic conductors, Ag2S type superionic conductors, and Ag3SI type superionic conductors are introduced. It is reviewed in the section 1.4 that the p-d hybridization is deeply concerned in the superionicity in those type superionic conductors. The section 2 is devoted to the review of the electronic state studies for nano-ionics using the DV-Xα cluster method. As this method is very convenient for many scientists, it is used in many complicated materials,
such as superionic glasses. In the section 2.1, the electronic state studies by making use of the both diagram of overlap population and bond overlap population are introduced. It is introduced in the section 2.2 that the covalency of noble metal halides is in the border between that of the fourfold coordinated compounds such as AgI and that of the sixfold coordinated compounds such as AgCl. The last section is devoted to the studies on the multi-pole polarizabilities of closed p- and d-shell ions.

1. Electronic structure of superionic conductors
1.1 Electronic structure of AgI type superionic conductors

Experimental studies of thin films of silver monofluoride indicated that its optical properties differed in significant ways from those of the other silver halides. Then Birtcher et al. [1] tried calculations for the valence states of AgF using the LCAO method. It was seen that the peculiar features of the AgF measurements could be understood since the 4d valence band of Ag⁺ was found to lie above the 2p valence band of F⁻, and was hence the highest occupied band.

Smith [2] applied the modified tight binding approach to calculate the electronic structure of the silver iodide polymorphs. The four phases which he investigated were the α, β and γ modifications and the high pressure polymorph having the NaCl structure. The ionicity values obtained for three different phases agreed well with the values of Phillips [3] derived from the dielectric data and the computed band structures were in good agreement with independent pseudopotentials. Smith also applied the pseudopotential calculations to AgI [4]. The resulting band-structure for the metastable phase with the zinc-blende structure, γ-AgI, was in good agreement with that described above [2].

Goldmann [5] reviewed detailed experimental and theoretical informations of the valence and conduction band states in CuCl, CuBr, CuI, and AgI. He checked their consistency to extract one unifying interpretation. A band structure model was proposed based upon photoelectron spectroscopic data. It was able to interpret all available experimental information from optical absorption spectroscopy, soft X-ray absorption and emission spectroscopy and the photoelectron data.

Ostrow and Goldmann [6] measured temperature dependent photoelectron spectra of AgI. The spectra were decomposed into approximate partial p and d densities of valence states by using atomic cross sections for the corresponding partial photoexcitation probabilities.

Self-consistent Hartree-Fock calculations were performed for AgF, AgCl and AgBr in the fcc phase by Kunz [7]. Qualitatively these results agreed well with other calculations for these systems.
Akopyan et al. [8] also reviewed the following optical spectroscopy of superionic conductors. The Brillouin zone symmetry of both wurtzite and zincblende structures allows the $p$-$d$ mixing throughout the zone, in contrast to the rock-salt structure of AgCl and AgBr where mixing cannot occur at $k = 0$. The $p$-$d$ hybridization in AgI is due to the $\Gamma_{15}$-components of the d-states, while the $\Gamma_{12}$-components remain isolated. The degree of the $p$-$d$ hybridization at $k = 0$ has been estimated from the spin-orbit splitting of the $E_0$ excitons as 32% for Ag-4$d$ states and 68% for I-5$p$ states. The changes in the valence band in AgI associated with the phase transition to the $\alpha$-phase have been studied in [6]. A considerable broadening of the I-5$p$ band by about 0.3eV with an insignificant effect on Ag-4$d$ states has been found. The temperature dependence of the valence $p$-band width is shown in Fig.1. The changes in the photoemission spectra were interpreted as a result of the breakdown of the symmetry rules of the $p$-$d$ hybridization upon cation lattice melting. In the $\alpha$-phase the $p$-$d$ admixture is allowed for all d-state band.

![Figure 1](image)

**Figure 1.** $p$-band width of AgI as a function of temperature [8].

Takahashi et al. [9] investigated the electron density distribution in $\beta$-AgI on the basis of X-ray intensity data obtained by single crystal diffractometry. They indicated that $\beta$-AgI is not a highly ionic-bonded compound from several broad peaks observed on the difference Fourier map. They also indicated that the charge accumulation on Ag-I bond along the c-axis explained the existence of a low energy excitation mode. The bonding nature in $\beta$-AgI is schematically illustrated in Fig.2.
Figure 2. Schematic picture of the covalent and ionic charge distributions in wurtzite-type AgI. Large and small circles indicate I and Ag ions, respectively. Dots between Ag and I ions along the c-axis represent the molecular-like covalent bond. Broken lines denote the ionic bond [10].

The $L_1$ and $L_2$ X-ray absorption edges of iodine were measured in $\beta$- and $\gamma$-AgI at 11K and in $\alpha$-AgI at 460K by Angeretti et al. [11]. Although the two non-superionic phases were characterized by different diffraction patterns, their absorption spectra were very similar. They calculated the edge fine structures of $\beta$- and $\gamma$-AgI by a full-multiple-scattering formalism utilizing a complex potential. The relevant characteristics of the spectra were satisfactorily reproduced by taking into account only the first two coordination shells of iodine.

The fundamental optical absorption bands were found by Edamatsu et al. [12] at about 4.5eV in the alkali cuprous halides of $K_2CuCl_3$, $K_2CuBr_3$, $Rb_2CuCl_3$ and $Rb_2CuBr_3$, and from 3.9 to 5.2eV in $Rb_2CuI_3$. They concluded from the measured ultraviolet photoelectron spectra of these materials that the uppermost valence band of alkali noble-metal halides are the $d$-band of noble-metal ions and the $p$-band of halogen ions. The energy band structures of $K_2CuCl_3$ and $Rb_2AgI_3$ were calculated by the augmented plane wave (APW) method. It was shown that the direct band gap exists at the $\Gamma$ point in each crystal. The features of the calculated valence bands were consistent with the optical absorption and the photoelectron spectra.

Onwuagba [13] carried out the self-consistent local density calculations of the electronic structures for AgF, AgCl and AgBr by the tight binding linearized muffin-tin orbital-atomic sphere approximation method. He indicated that the silver $4d$ orbital strongly hybridizes with the halogen $p$
orbitals in the valence band and this performs a vital role in the configuration of the total density of states.

Ferhat et al. [14] also computed the electronic band structures and density of states of zinc-blende CuCl, CuBr and CuI using the tight-binding method.

Rakitin and Kobayashi [15] deliberated theoretically the mechanism of superionic transition in the framework of the chemical bond peculiarities approach which was originally proposed by Phillips [16]. They concluded that with allowance made for the electron-phonon interaction, the $p$-$d$ hybridization results in the appearance of the local potential minimum in addition to the lattice potential well. They also indicated that discrimination of superionic or non-superionic materials mainly by the strength of $p$-$d$ hybridization, considering that the appearance of the local potential minimum is the essential prerequisite for the superionic transition. We suppose that these studies have prompted to recent further works on the DOP and BOP (refer to chap.2) of materials.

Ab initio electronic structure calculations were presented for five photographically relevant silver halide crystals AgCl, AgBr, $\alpha$-AgI, $\beta$-AgI and $\gamma$-AgI by Victora [17]. Theoretical predictions for most observed features, such as bandwidths and the location of band gaps, were in good agreement with experiments. Although band-gap magnitudes were underestimated, the relative ordering of the direct gaps was correctly predicted for the five crystals.

Nunes et al. [18] calculated the electronic structures of silver halides AgCl, AgBr and AgI within the local density approximation using a pseudopotential, plane-wave method.

### 1.2 Electronic structure of Ag$_2$S type superionic conductors

To shed light on the electronic structures observed for Ag chalcogenides, Hasegawa [19] carried out the the augmented-plane-wave (APW) calculations for some hypothetical crystalline compounds.

Gordienko et al. [20] calculated self-consistently the band structure and charge density of the silver halides by the density functional method using norm-conserving pseudopotentials. The top of valence band and the bottom of conduction band for AgI with the zinc-blende structure were realized at the $\Gamma$ point, unlike with the other silver halides with rocksalt structure.

The electronic structure of Ag$_2$Te was investigated by Kashida et al. [21], theoretically using the self-consistent full-potential linear-muffin-tin-orbital (LMTO) calculation, and experimentally using photoelectron spectroscopy. It was found that the $\alpha$-$\beta$ phase transition was ascribed to the energy lowering accompanying the Ag coordination change and the atomic displacements in the $\beta$-Ag$_2$Te. The diffusion path of Ag ions was also studied and was consistent with that obtained by Kobayashi et al. [22] using MD simulation.
Barman et al. [23] investigated the electronic structure of Ag$_{2+\delta}$S single crystals as a function of temperature and nonstoichiometry, $\delta$.

1.3 Electronic structure of Ag$_3$SI type superionic conductors

The electronic band calculations of $\beta$-Ag$_3$SX (X=I, Br) were conducted in order to make the high ionic conductivity of silver ions clear using the tight-binding method by Kohda et al. [25]. The crystal structure of the $\beta$-Ag$_3$SI is shown in Fig.3. The $d$ bands of Ag ions were much more weakly coupled with the $p$ bands of halogen ions, while those of S ions were much more strongly coupled with the $d$ bands. The strength of $p$-$d$ hybridization was discussed to connect with the activation energy for the ionic conduction. It was shown that the high ionic conductivity of $\beta$-Ag$_3$SX (X=I, Br) primarily stems from the weakness of the $p$-$d$ hybridization. Namely, the difference of ionic conductivity of $\beta$-Ag$_3$SX (X=I, Br) was originated in the difference of strength of $p$-$d$ hybridization between Ag-I and Ag-Br.

![Figure 3. Crystal structure of $\beta$-Ag$_3$SI [25].](image)

Recently Shimosaka et al. [26] have studied the electronic structure of Ag$_3$SI using the LMTO band calculation method. They have shown that $\beta$-Ag$_3$SI (cubic antiperovskite structure) has a direct gap at M=(1/2,1/2,0), while the low-temperature $\gamma$-Ag$_3$SI has an indirect gap from M to $\Gamma$(0,0,0). The contour map of $\beta$-Ag$_3$SI, where Ag ions are assumed to move within the (001) plane, is found to reproduce the experimental results showing four energy minima at (1/2+0.14,1/2,0), as shown in Fig.4.
1.4 Estimation of $p$-$d$ hybridization

Kikuchi et al. [27, 28] have studied the electronic properties of a series of tellurides with the antifluoride structure. They have carried out the first-principle density-functional calculations for these systems using the linearized augmented plane-wave (LAPW) method. Fig. 5 shows the band structures of (a)Ag$_2$Te and (b)Cu$_2$Te. To elucidate the strength of the coupling for the $d$ bands and $p$ bands, they selectively shifted downward the $d$ band originating from the Ag $d$ states in Ag$_2$Te or the $p$ band from the Te $p$ states in Cu$_2$Te. They concluded that Ag$_2$Te and Cu$_2$Te have remarkably different degree of the $p$-$d$ hybridization and the $d$-bands of Ag ions are much more weakly coupled with the $p$-bands of Te ions.

After Kikuchi et al. [27, 28], Ono et al. [29, 30, 31] also tried band calculations of 6 kinds of compounds, AgCl, AgBr, $\gamma$-AgI and $\gamma$-CuX(X=halogen) using the LCAO method to get some rule. The upper region of valence band of AgX is mainly occupied by the $p$-band of X$^-$, while that of CuX is mainly occupied by the $d$-band of Cu$^+$. To reveal the strength of coupling between the $d$- and $p$-bands in the noble metal halides, they selectively shifted downward the $d$ band originating from the $d$ states of Ag$^+$ for the case of AgX and the $p$ band of X$^-$ for the case of CuX. Let’s take the average value of the $d$-band of Ag as $\lambda$ for the case of AgI for example. Next they again tried the band calculation with shifting down the term value of $d$-band by $\delta_0$ and take the average value of new $d$-band as $\lambda'$. The actual shift $\delta$ is...
Figure 5. Band structures of (a)Ag\textsubscript{2}Te and (b)Cu\textsubscript{2}Te, calculated at the equilibrium lattice constants [27]. Bethe’s notation is used for the irreducible representations. \(E_F\) denotes the Fermi energy.

Figure 6. The actual shift \(\delta\) versus the given shift \(\delta_0\) of the selective band for Ag\textsubscript{2}Te, Cu\textsubscript{2}Te and AgI [27].

given by \(\lambda - \lambda'\). In AgX, the two bands are so easily separable that the \(d\)-band of Ag\textsuperscript{+} preserves its localized nature from hybridization. On the other hand, CuX gives rise to strong admixture of the \(d\)-band of Cu\textsuperscript{+} and the \(p\)-band of X\textsuperscript{-}. These results are consistent with the results of Kikuchi et al. [27, 28]. When they write the relationship of \(\delta\) and \(\delta_0\) as

\[
\delta = (k_{p-d})^{-1} \delta_0,
\]

\(k_{p-d}\) represents the strength of \(p-d\) hybridization. We see that \(k_{p-d}\) has the maximum value for CuI and then the \(k_{p-d}\) values of CuBr, CuCl, AgCl, AgBr,
and AgI follow in sequence. If they trace this sequence reversely, it corresponds to the order of magnitude of observed ionic conductivity in low temperature phase (γ), namely

\[ \sigma(\text{AgI}) > \sigma(\text{AgBr}) > \sigma(\text{AgCl}) > \sigma(\text{CuCl}) > \sigma(\text{CuBr}) > \sigma(\text{CuI}). \quad (2) \]

The ionic conductivities for these kinds of superionic conductors were measured by many authors. Especially many measurements have been done for AgX and CuX (X=halogen). The ionic conductivity \( \sigma \) is generally described by an Arrhenius expression

\[ \sigma = \frac{C}{k_B T} \exp\left(-\frac{E}{k_B T}\right), \quad (3) \]

where \( E \) is the activation energy of ionic conduction, \( C \) the prefactor, \( k_B \) the Boltzmann constant, and \( T \) the temperature. Ono et al. prepared the values of the activation energy of each material from the experiments [32, 33]. They showed that CuI has a larger activation energy \( E \) and a stronger \( p-d \) hybridization (larger \( k_{p-d} \)), while AgI has a smaller \( E \) and a smaller \( k_{p-d} \), as shown in Fig. 7. Smaller value of the strength of \( k_{p-d} \) hybridization loosen the coupling of \( \text{Ag}^+ \) and \( \text{I}^- \) and then leads to the small activation energy state. This interprets the experimental results where the ionic conductivity of AgI is about ten times larger than that of CuI. This also gives the microscopic interpretation of the origin of superionicity. Table 1 concludes their results simply.

**Figure 7.** Relationship between the values of activation energy for ionic conduction and the values of \( k_{p-d}^{-1} \). \( k_{p-d} \) is defined by the ratio of actual shift \( \delta \) to given shift \( \delta_0 \) of the selective band, as defined by Eq.1 [29, 30, 31].
Table 1. Difference between Ag and Cu [29, 30, 31]

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic radius (Å)</th>
<th>Quadrupole</th>
<th>p-d hybridization</th>
<th>Conductivity σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>1.26</td>
<td>large</td>
<td>weak</td>
<td>large</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>0.96</td>
<td>Large</td>
<td>strong</td>
<td>small</td>
</tr>
</tbody>
</table>

2. **DV-Xα method for nano-ionics**

The DV-Xα method devised by Adachi et al. [34] is widely used all over the scientific area. Kowada et al. [35] applied this method to calculate the electronic states of α AgI-based superionic conductors. The electronic states of trivalent ion conductors M₂(WO₄)₃ (M=Al,Sc,Lu,Yb,Tm,Er,Y) were calculated by Imanaka et al. [36] using this method. Matsunaga et al. [37] performed the electronic state calculations on an interstitial cationic defect in AgCl and NaCl crystals using this method. Matsunaga et al. [38] also carried out molecular orbital calculations on an interstitial Ag in AgBr and AgI using this method.

2.1 **Diagram of overlap population**

Kowada et al. [39] have calculated the electronic states of AgI-based superionic conducting glasses using the DV-Xα cluster method [34] for the AgI₄ cluster shown in Fig.8. They used the Mulliken’s population analysis in order to get the orbital population and the overlap population [40]. The influence of the Madelung potential was included in their calculations.

![Figure 8. Structure of model cluster MI₄ [39].](image-url)
Figure 9(a) shows the diagrams of overlap populations (DOP) for AgI$_4$. The abscissa of DOP shows the magnitude of the anti-bonding and bonding nature of molecular orbitals in Ag-I bonding in the left-hand side and the right-hand side, respectively. From this DOP, we see that the upper valence band of the AgI$_4$ cluster is occupied by the 4$d$ band of Ag and the 5$p$ band of I with hybridization state. We also can see in the DOP of AgI$_4$ that there are the anti-bonding and bonding states included the $p$-$d$ hybridization in the upper valence band. The $p$-$d$ bond overlapping states include the negative anti-bonding states and the positive bonding states. These two bonding states cancel out each other and lead to the result of substantially weak bond overlapping states.

Figure 9(b) shows the DOP for NaI$_4$. This figure is significantly different from that found in AgI$_4$ (Fig.9(a)). Namely there is no anti-bonding contribution in the upper valence band of NaI$_4$. The nearly filled 4$d$ band of Ag and the 5$p$ band of I considerably overlap in the anti-bonding manner to bring about repulsive interactions.

By comparing Figs.9(a) and 9(b), we see that there exist both components of the anti-bonding and bonding in the DOP for AgI$_4$, while there exist only the bonding component in the DOP for NaI$_4$. The crucial difference of the DOP of AgI$_4$ and NaI$_4$ is in the existence of the 4$d$ band of Ag$^+$ for AgI$_4$.

Recently Ono et al. [41, 42] and Kobayashi et al. [43] have calculated the electronic states of noble metal halides and alkali halides using the DV-X$\alpha$ cluster method [34] for the $A_1B_{14}$-cluster [41]. They used the Mulliken’s population analysis in order to get the orbital population and the overlap population. The influence of the Madelung potential was included in their calculations [41, 42].

**Figure 9.** Energy distribution of bond overlap population for AgI$_4$ and NaI$_4$ clusters. The energy scales are normalized as the Fermi energy to be 0eV [39].
Tomoyose et al. [44] have studied the electronic states of AgX (X=Cl,Br,I) and copper halides CuX using the DV-Xα cluster method. They have tested several model clusters to obtain the density of states and the bond overlap population (BOP). They found that the BOP of copper halides are larger than those of silver halides. These results are consistent with the Philips ionicity picture for $A^NB_{8-N}$ [16].

The highest lithium ionic conductivity has been reported for La$_{4/3-y}$Li$_3$Li$_2$O$_6$ (LLTO) with perovskite-like structure by Inoue and Zou [45]. They have tried to calculate the BOP of model clusters for LLTO using the DV-Xα cluster method. Their model clusters were LiO$_4$, LiO$_{12}$ and LiO$_{20}$. They have demonstrated that the increase of the bond order corresponds to the increase of covalent bonding between the Li$^-$ ion and surrounding O$_2^-$ ions.

### 2.2 Covalency of metal halide cluster

Phillips investigated the chemical bonding state of $A^NB_{8-N}$ type compounds by the analytical method [46, 16]. The covalent character is involved more or less in the diamond structure, zincblende structure and rock salt structure compounds. He found that the fourfold coordinated compounds and the sixfold coordinated compounds could be divided at the critical value of ionicity $f_c=0.785$. On the Phillips scale of ionicity, the noble metal halides have the values of ionicity shown in Table 2. The values of ionicity for noble metal halides lie close to the critical value $f_c=0.785$. This result indicates that the crystal structure of AgI can be easily transformed into the rock salt structure.

**Table 2.** Ionicity of noble metal halides [16, 46].

<table>
<thead>
<tr>
<th>Compound</th>
<th>CuI</th>
<th>CuBr</th>
<th>CuCl</th>
<th>CuF</th>
<th>AgI</th>
<th>AgBr</th>
<th>AgCl</th>
<th>AgF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionicity $f_i$</td>
<td>0.692</td>
<td>0.735</td>
<td>0.746</td>
<td>0.766</td>
<td>0.770</td>
<td>0.850</td>
<td>0.856</td>
<td>0.894</td>
</tr>
</tbody>
</table>

**Figure 10.** Structure of model cluster A$_{13}$B$_{14}$ [43].
under hydrostatic pressure [47, 48]. We have calculated the covalency of several compounds with the diamond structure, the zincblende structure and the rock salt structure using the DV-Xα cluster method [42]. Our calculation results of the BOP for noble metal halides are consistent with the Phillips’s results and the relation between the Born-Haber cycle and the Born-Lande equation. Namely, the noble metal halides lie close to the borderline between the fourfold coordinated compounds and the sixfold coordinated compounds except for AgF [42].

3. Multipolarizability

The multi-pole polarizabilities of closed $p$- and $d$-shell ions were calculated by Mahan [49]. Kikuchi et al. [27] normalized Mahan’s results in terms of Pauling’s radii to remove the nominal dependence on the dimension of ions. The quadrupole and octopole polarizabilities were scaled by the fifth- and seventh-power of the ionic radii, respectively. Those results for relevant cations are listed in Table 3. Here $\sigma_P$ is the Pauling’s ionic radius. $\alpha_q$ and $\alpha_o$ are the quadrupole and octopole polarizabilities given by Mahan [49], respectively.

The reduced values of polarizabilities give us the understandable deformability of the noble-metal ions. The reduced values of quadrupole polarizabilities for Ag$^+$ and Cu$^+$ are ten times larger than those for Li$^+$ and Na$^+$. This shows that the noble-metal ions are apt to deform compared with alkali ions. These things are summarized in Table 4.

Recently the dipole polarizabilities and deformation dipole tensors of ions in rock-salt structure alkali halides have been calculated by Michihiro et al.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>Coordination number</th>
<th>Quadrupole deformability</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>rocksalt</td>
<td>6</td>
<td>small small</td>
</tr>
<tr>
<td>AgCl</td>
<td>rocksalt</td>
<td>6</td>
<td>large large</td>
</tr>
<tr>
<td>AgI</td>
<td>wurtzite</td>
<td>4</td>
<td>large large</td>
</tr>
</tbody>
</table>

Table 3. Reduced multipole polarizabilities for closed-shell cations. The quadrupole and octopole polarizabilities, $\alpha_q$ and $\alpha_o$, for each cation are normalized in terms of the corresponding Pauling’s ionic radius $\sigma_P$ [27].

Table 4. Difference between NaCl and AgCl [29, 30, 31].
[50] with the local density approximation. The Szigeti effective charge also has been obtained from the deformation dipole tensor.

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