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**Kyoto University**
THEORETICAL STUDY ON ELECTRONIC STATES
OF POINT DEFECTS IN IONIC CRYSTALS

Katsuyuki MATSUNAGA

1997
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CHAPTER 1
GENERAL INTRODUCTION

§1.1 Introduction

In a perfect crystalline solid, all atoms are arranged in a periodic manner according to its crystal structure. However, this situation can only exist at the absolute zero of temperature, 0K. Above 0K, imperfections of the atomic arrangement occur because of thermodynamic reasons. Such imperfections are called intrinsic lattice defects. On the other hand, extrinsic point defects occur by the introduction of impurity atoms or the irradiation with x-ray and energetic particles into a crystalline solid. Among various kinds of intrinsic and extrinsic lattice defects, point defects have the simplest structure, which are generally present at a single atomic site in a crystalline solid. The point defects can have a great influence on the chemical and physical properties of a crystalline solid, such as mechanical strength, electrical conductivity, and chemical reactivity. Therefore, a large number of investigations on the point defects have been done in order to understand various phenomena of solids due to the presence of point defects.

By the presence of point defects in a crystal, the three-dimensional periodicity of the crystal is lost at their sites. Various phenomena occurring due to the point defects should have a close relationship with the specific atomic arrangement at point defects, which is different from that in a defect-free region of a crystal. Thus the electronic structures at point defects are expected to
greatly differ from those in the defect-free region. From a viewpoint of material design in future, detailed knowledge of electronic structures of point defects in a crystal should be useful and indispensable.

It is well known that the point defects in ionic crystals also give rise to their peculiar optical and electrical properties. Atoms in ionic crystals have their own effective charges to keep the whole system neutral. The point defects created by removal or addition of the ions are also expected to have the effective charges. The charged point defects produce electric fields locally, and thus extra electrons are possible to be trapped or released at the defects. In the case of positively charged point defects, such as F-centers and interstitial cations in this study, extra electrons can be trapped at the defect sites because of the positive Coulombic field of the defect, and characteristic electronic states are newly created in a wide band gap of ionic crystals. In order to understand various physical and chemical properties due to the defects, it is crucial to investigate the feature and role of the defect-originated states in detail.

For the purpose of understanding the microscopic features of point defects, a theoretical calculation on the electronic structures of point defects is a powerful tool. With the development of new theoretical methods and high speed computers, the first-principles calculations have been able to deal more accurately with electronic structures of point defects in a crystal. Among many kinds of the first-principles calculations, band-structure calculations with periodic boundary conditions require a large super cell in order to obtain electronic structures of point defects. On the other hand,
a cluster calculation is suitable to investigate localized imperfections. This is because a cluster calculation does not require any periodicity of crystals, and can be readily applied to any atomic arrangement near point defects. The discrete variational (DV) -Xα molecular orbital calculation [1,2] employed in the present study is one kind of cluster calculations. In this method, we construct a model cluster which includes several atoms around a point defect, and molecular orbitals in the cluster are calculated from the first principles. Theoretical backgrounds and computational procedure in the DV-Xα method will be introduced afterwards in this chapter.

The present study is focused on intrinsic and extrinsic point defects in ionic compounds. Firstly, we investigate F-centers in alkali halide crystals with the rock-salt structure in chapter 2. F-centers are one kind of color centers which are produced in alkali halides and metal oxides by additive coloration method, x-ray and γ-ray irradiation [3]. F-centers in alkali halides are regarded as the point defects consisting of an electron trapped in a halogen vacancy, as shown schematically in Fig. 1-1. Although alkali halides are normally transparent in visible light region, F-centers in alkali halides bring about photo-absorption in visible light region as a result of the excitation of the trapped electron, leading to the coloration of the crystals. The local atomic and electronic structures of F-centers have a close relationship with their optical absorption process, and thus have been of practical as well as purely scientific interest, because of the practical application to F-center laser [4], and a typical candidate for researchers in solid state physics.
In the present investigations on the F-centers, the feature of wave functions localized at F-centers is examined in detail. Photo-absorption energies due to F-centers are computed from the first principles, and are compared with experimental data previously reported. Moreover, the atomic relaxation around F-centers are estimated, and the relationship between the characteristic wave functions of F-centers and the local atomic structure is investigated.

Fig. 1-1 Structure of an F-center in alkali halide crystals with rock-salt structure.

Secondly, intrinsic point defects in alkali and silver halide crystals are examined in chapter 3. In alkali halides, cation vacancies are commonly encountered in thermal equilibrium (Schottky-type defects). While interstitial Ag$^+$ ions are dominant in silver halides (Frenkel-type defects). The schematic illustrations of these types of point defects are shown in Fig. 1-2. Table 1-1 lists formation-enthalpy values, $h_F$, for Schottky- and Frenkel-type point defects in these crystals [5]. In the cases of silver halides, the formation enthalpy of interstitial Ag$^+$ ions can be
recognized to be small, even compared to that of cation vacancies in alkali halides.

![Diagram of NaCl and AgCl with intrinsic point defects](image)

**Fig. 1-2** Intrinsic point defects created in NaCl and AgCl.

**Table 1-1** Experimental values of formation enthalpy for Schottky-type and Frenkel-type point defects.

<table>
<thead>
<tr>
<th>Defect type</th>
<th>Compound</th>
<th>$h_F$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky defects</td>
<td>LiF</td>
<td>2.34</td>
</tr>
<tr>
<td></td>
<td>LiCl</td>
<td>2.12</td>
</tr>
<tr>
<td></td>
<td>LiBr</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td>LiI</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>NaCl</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>KCl</td>
<td>2.26</td>
</tr>
<tr>
<td>Frenkel defects</td>
<td>AgCl</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>AgBr</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>$\beta$-AgI</td>
<td>0.70</td>
</tr>
</tbody>
</table>

In the present study, the origin of formation of an intrinsic interstitial Ag ion in AgCl crystals is pursued from the viewpoint of chemical bonding state around an interstitial Ag. The presence of an interstitial Na ion in NaCl is hypothetically considered, and we make a comparison between an interstitial Na and an interstitial Ag. Formation of strong covalent bonds around an
interstitial Ag ion is pointed out, and the relationship with photographic phenomena of AgCl is discussed.

In chapter 4, electronic states of interstitial Ag ions in AgBr and AgI, which are commonly used as photographic materials, are investigated. It is well known that interstitial Ag ions in silver halides play an important role for their photographic phenomena [6,7]. The phenomenological mechanisms for photographic processes have been established by Gurney-Mott [8], Mitchell [9] and Hamilton [6,7], which will be introduced in chapters 3 and 4. According to their mechanisms, when silver halides are irradiated by visible light, interstitial Ag ions form Ag clusters, which are an origin of latent images during photographic processes. However, theoretical calculations on the formation of Ag clusters in silver halides have been little done, in spite of their importance. Electronic structure calculations in the realistic systems of AgBr and AgI are required for further understanding of the mechanism of the Ag-cluster formation.

Chapter 5 is also devoted to a further discussion on the Ag-cluster formation in AgBr and AgI. The previous mechanisms emphasize that Ag clusters are formed by aggregation of interstitial Ag ions. This indicates that the interaction between interstitial Ag ions is significant in the Ag-cluster formation. In accord with the above mechanism, the chemical bonding state of aggregating interstitial Ag ions and the interaction between the Ag interstitials are investigated. It is shown that the present analysis on the chemical bonding state around Ag interstitials in silver halides provides a good description about the mechanism of the Ag-cluster formation and the photosensitivity.
§1.2 Discrete Variational Xα Method

1.2.1 Theoretical backgrounds and computational procedure

First-principles molecular orbital (MO) calculations have been carried out using the discrete variational (DV) Xα method [1,2]. The DV-Xα method is based on the Hartree-Fock-Slater (HFS) model [10]. The one-electron HFS equation for the molecular orbital, $\phi_k(r_k)$, is given as [10],

$$\left[ -\frac{\nabla^2}{2} + V_{\text{eff}} \right] \phi_k(r_k) = E_k \phi_k(r_k), \quad (1-1)$$

where

$$V_{\text{eff}}(r_k) = -\sum_v \frac{Z_v}{|r_k - R_v|} + \int \frac{\rho(r')}{|r_k - r'|} dr' + V_{\text{xc}}(r_k). \quad (1-2)$$

Here, $r_k$ is one of sampling points in the calculations. In eq. (1-2), the first term is the attractive potential from the nucleus located at $R_v$, where $Z_v$ is the atomic number. The second term is the electronic Coulomb repulsion potential, and $\rho(r')$ is the electronic charge density at the point $r'$. The exchange-correlation interaction, $V_{\text{xc}}$, between electrons is expressed as [10]

$$V_{\text{xc}}(r) = -3\alpha \left( \frac{3}{4\pi} \rho(r) \right)^{\frac{1}{3}}, \quad (1-3)$$

where $\alpha$ is the parameter fixed at 0.7 throughout the present work, whose value is empirically applicable for most of atoms [1].
MOs obtained by calculations are represented by the linear combination of atomic orbitals (AOs), $\chi_i(r_k)$, i.e.,

$$\phi_k(r_k) = \sum_i C_{ik} \chi_i(r_k)$$  \hspace{1cm} (1-4)

For the basis sets, we employ the numerical AOs, $1s-np$ for alkali atoms, $1s$ to $md$ for halogen atoms, and $1s-4p$ for an Ag atom, where $n$ and $m$ are the principal quantum numbers of the highest occupied AOs for alkali and halogen atoms, respectively. These AOs are numerically calculated by solving the atomic Hartree-Fock-Slater equation so as to be optimized for given chemical environment.

The self-consistent MO wave function and MO levels are obtained by solving the secular equation,

$$HC = \varepsilon SC$$  \hspace{1cm} (1-5)

The matrix elements of hamiltonian, $H_{ij}$, and overlap integrals, $S_{ij}$, are evaluated by the DV numerical integrations, as follows,

$$H_{ij} = \sum(k) \omega(r_k) \chi_i^*(r_k) H(r_k) \chi_j(r_k)$$  \hspace{1cm} (1-6)

$$S_{ij} = \sum(k) \omega(r_k) \chi_i^*(r_k) \chi_j(r_k)$$  \hspace{1cm} (1-7)

where $\omega(r)$ is the reciprocal of the sampling point density at $r_k$. The eigenvalue problem of eq. (1-5) are solved, providing orbital eigenvalues and eigenfunctions.
Mulliken population analysis [11] is employed in order to obtain the orbital population, $Q_j^l$, and the overlap population, $Q_{ij}^l$, at the $l$-th MO, given by

$$Q_{ij}^l = f_i C_{il} C_{jl} \sum_k \omega(r_k) \chi_i(r_k) \chi_j(r_k), \quad (1-8)$$
$$Q_i^l = \sum_j Q_{ij}^l, \quad (1-9)$$

where $f_l$ is the number of electrons at the $l$-th MO level. The sum of $Q_i^l$ on an atom A becomes the effective charge of the atom A. Then the net charge of the atom, $n_A$, is expressed as,

$$n_A = Z_A - \sum_l \sum_i Q_i^l, \quad (1-10)$$

where $Z_A$ is the atomic number. The sum of $Q_{ij}^l$ between two atoms A and B makes a bond overlap population (BOP), $N_{A-B}$, i.e.,

$$N_{A-B} = \sum_l \sum_{i,j} Q_{ij}^l, \quad i \in A, j \in B. \quad (1-11)$$

The BOP is a good measure of strength of a covalent bond between atoms. By using these values, ionicity and covalency in the clusters are able to be quantified.
In an ionic crystal with any structure, arrangements of charged atoms yield the electrostatic potential. The electrostatic potential should have a great influence on electronic structures of ionic crystals. In particular, molecular orbitals in model clusters for ionic crystals are largely affected by the electrostatic potential constructed by ions surrounding the clusters [12]. Thus, in this section, the electrostatic potential in ionic crystals is reviewed, and the computational method of the electrostatic potential employed in the present calculations is introduced.

In an infinite lattice with any structure composed of point charges, the electrostatic potential at any site of the lattice, \( V_{es} \), is given by the direct sum of Coulomb interactions as

\[
V_{es} = \sum_{j} \frac{Z_j}{r_j} ,
\]

(1-12)

where \( r_j \) is the distance to the \( j \)-th point ion owning the \( Z_j \) charge. The \( V_{es} \) at any lattice site due to all charges except the one at that point is expressed in terms of the Madelung constant, \( \alpha_m \), and the shortest distance between unlike ions, \( r_0 \),

\[
V_{es} = \pm \alpha_m \frac{Z_0}{r_0} , \quad Z_0 = \left| Z_j \right| .
\]

(1-13)

Here, the positive value of \( V_{es} \) is the one at the any anion site, and the negative at any cation site. The accurate values of \( \alpha_m \) for three types of crystal structures [13,14] are listed in Table 1-2, where the shortest distance between unlike ions is the characteristic
length for the Madelung constants. The values of $\alpha_m$ are dependent only on the geometry of each lattice.

Table 1-2 Values of Madelung constants for three types of crystal structures.

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Madelung constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1.74756</td>
</tr>
<tr>
<td>CsCl</td>
<td>1.76267</td>
</tr>
<tr>
<td>zinc blend</td>
<td>1.63806</td>
</tr>
</tbody>
</table>

In the present cluster calculations, model clusters used are embedded in a finite lattice composed of point charges, in order to take account of the electrostatic potential due to ions outside clusters [15]. A finite lattice of point charges for any crystal structure is constructed by extension of the unit cell using the translational vectors. However, the values of $\alpha_m$ obtained from a finite lattice are, in general, slow to converge to the accurate values in Table 1-2, even when the size of a finite lattice is taken to be large enough. The Evjen's method [16] is often used in evaluating values of $\alpha_m$ for a finite lattice. In this method, the electrostatic potential of a finite lattice is calculated by the direct sum of Coulomb potentials due to point charges. A rapid convergence can be attained for a neutral group of ions with any specific crystal structure, if necessary taking fractional charges. Table 1-3 shows values of $\alpha_m$ at an anion site for three types of
crystal structures obtained by the Evjen's summation method, where the electrostatic potentials over 9 or 11 cubic shells are summed up. In the case of the rock-salt structure, a good agreement with the accurate value in Table 1-2 can be attained. However, the values of $\alpha_m$ for CsCl and zinc-blend structures are found not to attain a convergence to the accurate one in Table 1-2. The difference from the accurate values is considerably large. Coker pointed out that these results are originated from a residual potential produced by a finite lattice of point charges [14].

Table 1-3 Values of Madelung constants at an anion site calculated by the Evjen's summation method.

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Madelung constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9 shells</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.74756</td>
</tr>
<tr>
<td>CsCl</td>
<td>3.12200</td>
</tr>
<tr>
<td>zinc blend</td>
<td>4.63620</td>
</tr>
</tbody>
</table>

1.2.3 Evaluation of residual potential

The residual potential pointed out by Coker is introduced. In a unit cell of NaCl and CsCl-type structures, two types of ions are involved, whose charges are equal in magnitude but of opposite sign. As a typical example, a unit cell of CsCl structure is shown in Fig. 1-3. The two types of ions in each unit cell can be grouped together to form an electric dipole. In a finite crystal lattice where
a central unit cell is symmetrically surrounded by a number of complete unit cells, all dipoles are added in the same sense, and thus an average electric field due to dipoles can be considered to exist within the lattice. Coker discussed that the residual potential due to the dipoles causes the trouble in the convergence of the direct sum of Coulomb potentials.

![Diagram of a pair of cation and anion in the unit cell of CsCl structure.](image)

Fig. 1-3 A pair of a cation and an anion in the unit cell of CsCl structure.

The electric field produced by a dipole at a long distance is expressed as

\[
\text{d}E = \frac{\sigma \mathbf{r}}{r^3} \, dv
\]

(1-14)

In this equation, \( \sigma \) is a magnitude of dipole moment per unit volume, given as

\[
\sigma = \frac{\mu}{abc}
\]

(1-15)
where \( a, b \) and \( c \) are unit-cell lengths. From eq. (1-14), Coker analyzed an electric field due to dipoles in finite lattices with various orthorhombic crystal structures. At the midpoint of the pair of ions in the central unit cell, \( r_d \), he obtained the electric field produced by surrounding dipoles as follows [14]

\[
E_x = \frac{8\mu_x}{abc} \tan^{-1}\left(\frac{bc}{a\sqrt{a^2 + b^2 + c^2}}\right), \quad (1-16)
\]

where \( \mu_x \) is a dipole moment along \( x \) axis per unit volume. \( E_y \) and \( E_z \) are obtained from \( E_x \) by cyclic permutation of \( a, b \) and \( c \). Thus, there is a gradient of potential due to dipoles in a finite lattice, and each ion is subjected to such electric field. Finally, the dipole potential in the vicinity of \( r_d \) is given as

\[
V_{dip} = -E (r - r_d) \quad . \quad (1-17)
\]

It was suggested that the rapid convergence of Madelung potential for any finite crystal lattice can be attained by removal of the dipole potential from the direct sum of Coulomb potentials. In the case of the rock-salt structure, the dipole moment in each unit cell, \( \mu \), becomes zero. Therefore, the dipole potential does not contribute to the Madelung potential for the rock-salt structure.

Table 1-4 indicates the Madelung constants for several structures obtained in this way. In the present calculations, 11 shells around the central unit cell are included. All calculated values in Table 1-4 can be recognized to agree with those previously reported in Table 1-2, within the accuracy of 0.04%. In the present cluster calculation, model clusters are embedded in
the electrostatic potentials obtained in this way, and the molecular orbitals are calculated.

Table 1-4  Madelung constants obtained by removal of the dipole potential in a finite lattice.

<table>
<thead>
<tr>
<th>Lattice</th>
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</tr>
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<tbody>
<tr>
<td>NaCl</td>
<td>1.74756</td>
</tr>
<tr>
<td>CsCl</td>
<td>1.76199</td>
</tr>
<tr>
<td>zinc blend</td>
<td>1.63797</td>
</tr>
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</table>
CHAPTER 2
ELECTRONIC STATES OF F-CENTERS IN ALKALI HALIDE CRYSTALS

§2.1 Introduction

Alkali halides are typical ionic compounds, and a number of works have been achieved on their properties such as optical properties. Especially, photo-absorption as well as formation mechanism [3,17] of color centers in alkali halides have been studied for more than 60 years, and one of interests has been on the atomic and electronic structure of color centers. Among many kinds of color centers, F-centers are one of the simplest defects which are produced by x-ray or γ-ray irradiation, and give rise to the photo-absorption in visible light region of the spectrum. The F-center is regarded as a defect consisting of one electron trapped in a halogen-ion vacancy. Distinct optical features of F-centers, such as electronic excitation or emission process, are related closely to their electronic structure and interaction with surrounding ions. By making use of their optical absorption and emission processes suitable for laser operation, F-centers in ionic crystals are practically applied to the F-center laser [4].

Dawson and Pooly [18] and other many workers (see the review of ref. 3) have reported exprimental data of F-band energies for alkali halides. Ivey and Mollwo [19] pointed out that the F-band energies are approximately proportional to the inverse square of the lattice parameter, i.e., the Mollwo-Ivey's law. They
explained the origin of this law; in an F-center, one electron is in a bound state to a halogen-ion vacancy. Its wave function can be represented by that of a particle in a deep potential well, and is well localized around the vacancy. Therefore, the F-band energies which correspond to the transition to higher excited states have the above correlation with the lattice parameter.

There have been a number of theoretical studies of the F-centers in alkali halides and alkaline-earth oxides, focusing either on the optical transition, or on the lattice relaxation determined from the total energy of the defect system. In early days, simplified calculations using the point-ion model were carried out on the F-band energies for alkali halide crystals by Gourary and Adrian [20]. Öpic and Wood [21,22] performed the calculations on F-band energies for alkali halides, which are based on a Hartree-Fock calculation for a defect-centered inner region. They calculated the configuration-coordinate diagram for an F-center. In recent years, Klein et al. [23] applied the muffin-tin Green function method on the band structure calculation by augmented-plane-wave (APW) technique, in order to calculate the F and F+ centers in MgO. Their results agreed with the experimental data qualitatively, and they concluded that the atomic relaxation effects need to be included in the calculation. From the total energy viewpoint, Pandy and Vail [24], and Vail [25] made theoretical calculations of these defects. They combined an unrestricted Hartree-Fock cluster calculation with a classical static calculation for the rest of the lattice by a shell model. The atomic relaxation around the defect was determined by minimization of the total energy. These authors found that the nearest neighbor cations
relax by moving toward the F-center. Their optical transition energies showed decent agreement with the experimental values. Wang and Holzwarth [26], and De Vita et al. [27] used a pseudopotential supercell technique to evaluate the atomic relaxation around an oxygen-vacancy defect in MgO. Wang and Holzwarth also obtained the optical transition energies of F-centers, which are in good agreement with the experimental ones. However, these calculations have been done only for the ground state electronic configuration. Most recently, Surh et al. [28] calculated the optical transition energy of an F-center in LiCl, using a pseudopotential Green function method with the electron-hole interaction correction which arises from the transition of a bound electron. Their calculated excitation energy well agreed with the experimental one.

As stated above, a number of calculations have been developed in order to obtain physically meaningful results on the electronic structure of F-centers, thereby the optical transition energy and the lattice relaxation around these defects have been evaluated. In the present study, we make the first principles molecular orbital calculation on the electronic structure of the F-center in alkali halides using the DV-Xα method [1,2] for model clusters. This is the first time to perform the molecular orbital type of cluster calculation to evaluate the optical absorption energies from first principles. The prime objective of this study is to obtain physical insight to the defect-originated photo-absorption process in alkali halides with rock-salt structure. The molecular orbital calculation on small model clusters is extremely useful for this purpose in comparison with the band structure calculation.
The present calculation has been carried out using nearly minimal basis sets for reproducing optical transition energies quantitatively. Numerical atomic orbital basis functions which are optimized for given chemical environment are employed as a basis set. The use of this type of basis set has a great advantage when we need to calculate a number of elements in the periodic table in a first-principles manner. Additional defect basis-functions are not particularly included except numerical atomic orbital basis functions of surrounding ions. Molecular orbitals which localize at a defect are, therefore, composed of atomic orbitals of surrounding ions. We can eliminate the uncertainty associated with the generation of hypothetical defect orbitals. The optical transition energy is evaluated by the Slater's transition state method [10] in which the electronic relaxation associated with the electronic transition is taken into account.

In this study, we carry out a systematic study of F-centers for all alkali halides with rock-salt structure. The previous works by modern methods in recent years have focused on one or two materials (for example, NaF, MgO). Particularly, calculations of F-centers in compounds with ions of a large atomic number (Br⁻, I⁻ or Rb⁺) have not been reported by modern methods. Therefore, we apply our cluster calculation to all alkali halides, and make a detailed analysis on the defect-originated electronic states in these compounds. The relativistic effect is not taken into account. Firstly, the feature of wave functions localized at an F-center is examined in detail, and the F-band energies for all alkali halides are calculated. Secondly, the atomic relaxation around F-centers is investigated. The magnitude and direction of atomic relaxation
around an F-center are estimated from the calculation of the transition energy as a function of the displacement of nearest neighbor cations for all alkali halides.

§2.2 Computational Procedure

Figure 2-1 shows the structure of a model cluster used in the present work. This cluster (\((M_{14}X_{13})^+\)) consists of six cations of the 1st neighbors from the central anion of the cluster, and twelve anions and eight cations as the 2nd and the 3rd neighbors. In the case of the cluster containing a defect, a halogen vacancy is introduced by removing the anion located at the center of the cluster (i.e., \((M_{14}X_{12})^{2+}\)), and then one electron is added to the cluster (\((M_{14}X_{12})^+\)) as a model for the F-center.

![Fig. 2-1](structure.png)

Fig. 2-1  Structure of a model cluster (\((M_{14}X_{13})^+\)) used in this work. Closed and open circles denote the alkali ion \(M^+\) and the halogen \(X^-\), respectively. In the case of a defect cluster, a halogen vacancy is introduced by removing the anion located at the center of the cluster (\((M_{14}X_{12})^{2+}, (M_{14}X_{12})^+\)).
The interatomic distances in the cluster are employed from the experimental data for each crystal [29]. In the calculation, each cluster is embedded in a lattice composed of alternate point charges of $e^-$ and $e^+$ in order to add the electrostatic potentials due to the ions outside the cluster, as stated in chapter 1.

§2.3 Results and Discussion

2.3.1 Valence band structure and vacancy levels

We first investigate the valence electronic states of alkali halide crystals, by taking the cluster model of KCl as a typical example. Figure 2-2(a) exhibits energy levels of the defect-free cluster, $(K_{14}Cl_{13})^+$. The valence levels indicated by solid lines are occupied and are essentially composed of Cl-3s, 3p. The K-3p levels accidentally coincide with the Cl-3s band in the case of KCl. The lower part of the empty states (dashed lines) consists mainly of K-4s, 4p, and Cl-3d components. These occupied levels make the valence band and the unoccupied levels the conduction band. The energy separation between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) is 8.61 eV, which is in good agreement with the band gap experimentally obtained 8.6 eV [29].

Figure 2-2(b) displays the valence levels of a $(K_{14}Cl_{12})^{2+}$ cluster including a Cl- vacancy. By the introduction of the vacancy, two characteristic states, $16\alpha g$ and $24\tau_{1u}$, which can be referred to as the vacancy levels are created in the band gap. The energy levels shift lower than those of the defect-free cluster, because the anion vacancy has effectively a positive charge to
interact attractively with electrons. In this case, the $16\alpha_{1g}$ level is situated considerably low, so that an electron occupies this level, if we suppose an electron transfers from the outside of the cluster.

![Diagram](image)

**Fig. 2-2** Valence levels of the model clusters for KCl, where the (a), (b) and (c) are of the defect-free cluster, the cluster with an anion vacancy, and that with an F-center, respectively. Solid lines denote the energy levels of occupied states, and broken lines unoccupied states. Note that the F-center state $\alpha_{1g}$ appears within the band gap in Figs. (b) and (c).
When an extra electron is added to the \((K_{14}Cl_{12})^{2+}\), the level structure of the F-center cluster, \((K_{14}Cl_{12})^+\), is shown in Fig. 2-2(c). In this case, the \(16\Gamma_{1g}\) level is occupied by an electron. We can say that this electron is trapped by the defect, because these vacancy states have rather localized character at the vacancy. At the same time, the shift of the energy levels in Fig. 2-2(b) is recovered. The contour map of the \(16\Gamma_{1g}\) wave function on the (001) plane around the F-center is shown in Fig. 2-3(a). The \(16\Gamma_{1g}\) level is composed mainly of the nearest neighbor K-4s and 4p orbitals, and is the s-like orbital. By the removal of Cl\(^{-}\), the potential gradient of local electric fields toward the center of the defect is induced, which brings about the electronic polarization toward the vacancy in the \(16\Gamma_{1g}\) orbital. Originally K-4s and 4p orbitals make conduction band in the defect-free cluster. However the energy level of the \(16\Gamma_{1g}\) is shifted down from the conduction band (Fig. 2-2(c)) because the \(16\Gamma_{1g}\) orbital extends in part in the direction of the potential gradient as is seen in Fig. 2-3(a).

Fig. 2-3  Contour maps of wave functions of an F-center on the (001) plane in KCl. (a) \(16\Gamma_{1g}\) and (b) \(24\Gamma_{1u}\).
2.3.2 Calculation of photo-absorption spectrum

The level structure of the F-center cluster shows that the creation of the vacancy states causes an optical transition in visible light region. The optical absorption of F-centers is induced by the electronic transition from the $16a_{1g}$ to the excited states. Figure 2-4 shows the experimental spectrum for an F-center of KCl [30] and the calculated one by the present cluster calculation.

Fig. 2-4 Comparison of the experimental and theoretical optical absorption spectrum of an F-center in KCl. The upper shows the spectrum experimentally observed [30].
Photo-absorption cross-section is calculated from the first principles as follows: The oscillator strength \( I_{ij} \) for the electronic dipole transition for photo-absorption between states \( i \) and \( j \) is given by

\[
I_{ij} = \frac{2}{3} E_{ij} \left| \langle \phi_i | r | \phi_j \rangle \right|^2 ,
\]

(2-1)

where \( E_{ij} \) denotes the transition energy. In the present work, \( I_{ij} \) is obtained directly by the numerical integration of the dipole matrix element [31]. In the X\( \alpha \) model, the accurate energy for the electronic transition cannot be evaluated by the energy separation of the ground state, but such a transition energy can be calculated more accurately using Slater's transition state [10] where half an electron is removed from the initial level, \( \phi_i \), and is put in the final level, \( \phi_j \). This concept covers orbital relaxation effects, leading to an accurate evaluation of the transition energy [31]. In addition, the transition probability is also approximately obtained using the initial and final orbitals in the transition state [32].

As mentioned above, the \( 16a_{1g} \) orbital is mainly composed of the nearest neighbor K-4s, 4p orbitals. Therefore, the \( 16a_{1g} \) can be approximated by a linear combination of K-4s and 4p orbitals. As is seen in Fig. 2-3(a), the contour map of the \( 16a_{1g} \) shows large amplitudes around the nearest neighbor K. We can say that an electron in the F-center resides on the six nearest neighbor K atoms. Therefore, when we consider the electronic transition from the \( 16a_{1g} \), transition probabilities from 4s and 4p atomic orbitals of the nearest neighbor K atoms to higher molecular orbitals are taken into account. Then the oscillator strength is
evaluated for \( \langle \chi_{4s} | r | \phi \rangle \) and \( \langle \chi_{4p} | r | \phi \rangle \), and their sum weighted by the linear combination coefficients is approximately obtained as the total oscillator strength, i.e.,

\[
I_{ij} = \frac{2}{3} E_{ij} \sum_i \left[ c_{i1} \langle \chi_{i,4s} | r | \phi_j \rangle + c_{i2} \langle \chi_{i,4p} | r | \phi_j \rangle \right]^2 . \tag{2-2}
\]

The calculated spectrum is obtained assuming a Gaussian distribution for each peak as

\[
I(E) = \sum_j \frac{I_{ij}}{\sqrt{2 \pi} \sigma_j} \exp \left( -\frac{E - E_{ij}}{2 \sigma_j^2} \right) . \tag{2-3}
\]

where \( \sigma_j \) is the peak width. The peak width \( \sigma_j \) is chosen to be 0.2 eV so as to fit the experimental spectrum. The calculated spectrum shows three peaks in this energy region. The largest peak corresponds to the F-band, which is due to the transition to \( 24t_{1u} \) (see Fig. 2-2(c)). Under the \( Oh \) symmetry, the transitions from \( a_{1g} \) to \( t_{1u} \) states are allowed in terms of group theory. This transition indeed provides highest intensity. Figure 2-3(b) shows the contour map of the \( 24t_{1u} \) wave function. This state is of the \( p \)-like orbital. Therefore, the transition from \( 16a_{1g} \) to \( 24t_{1u} \) can be a dipole transition, and the energy difference between \( 16a_{1g} \) and \( 24t_{1u} \) levels will correspond to the F-band energy \( (E_a) \). In the present calculation, no other \( t_{1u} \) levels, to which the transition from the \( 16a_{1g} \) is allowed, are found in the energy region of Fig. 2-4. However, a small peak which is known as K-band appears in the experiment [33]. For example, \( d-d \) transitions of a transition metal ion in a complex are observed experimentally, in spite of
forbidden transitions by selection rules. Such $d-d$ transitions are thought to arise from a distortion of the symmetry of a complex or an asymmetrical vibration of a complex. In the present case, we employed the following assumption in eq. (2-2): The distance between the nearest neighbor K atoms is relatively large, and the $16a_{1g}$ can be considered to be localized on each of six nearest neighbor K atoms. Therefore, the transition from the $16a_{1g}$ is assumed to be that from $4s$ and $4p$ atomic orbitals of each nearest neighbor K atom. As a result of this assumption, small transition probabilities to $12t_{2u}$ and $17t_{2g}$ are found to appear in Fig. 2-4 (P and Q), although such transitions are forbidden by the group theory. These small peaks correspond to K- and L1-bands experimentally observed respectively, according to the classification by Lüty [33]. For the higher energy region, other small peaks, which are reported by the experiment [33], are also found by this calculation, and we find these bands associated with the F-center.

The photo-absorption energies $E_a$ by the transition state calculation for NaCl-type alkali halides together with the experimental data [3,18] are plotted against the lattice parameter ‘$a$’ in Fig. 2-5. The solid line in the figure denotes the relation obtained from the regression fitting with experimental data by Dawson and Pooly [18], which is expressed as

$$E_a = (60.5 \pm 9.8) a^{-1.81\pm0.10}$$  \hspace{1cm} (2-4)
Fig. 2-5 Dependence of the photo-absorption energies, $E_a$, on the lattice parameter, $a$, for various alkali halides with NaCl-type structure. Closed circles denote the experimental data [18], and open circles are of those computed in the present work for a case without displacement of ions around F-centers. The solid line is obtained from the fitting with the experimental data [18].

In eq. (2-4), $E_a$ and $a$ are in eV and Å, respectively. A similar relation can be simply derived from the particle-in-a-box type model [34]. In the model, the energy solution for an electron in the cubic box of a volume $a^3$ surrounded by infinite potential barriers is obtained from the well-known relation as

$$E = \frac{\pi^2(i^2 + j^2 + k^2)}{2a^2}, \quad (2-5)$$
in atomic units, where \( i, j \) and \( k \) are positive integers. The transition energy from the ground state \((i = j = k = 1)\) to the 1st excited state \((L^m_m, n^m_m) = (2,1,1), (1,2,1) \) or \((1,1,2)\), \(E_a\), is given as

\[
E_a = \frac{3\pi^2}{2a^2} \tag{2-6}
\]

This relation agrees approximately with eq. (2-4) as well as that of the Mollwo-Ivey's law. However, the model is not applicable to the analysis of detailed electronic structures, though it is valid for a rough estimation of F-band energies.

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<td>(2.41)</td>
<td>(2.04)</td>
<td>(1.85)</td>
<td>(1.71)</td>
</tr>
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</table>
Values of the transition energy computed in this work together with experimental values are listed in Table 2-1. The computed values for alkali halides with relatively small anions agree well with the experimental data. However, iodides, bromides and some chlorides exhibit much lower values compared with the experimental data. The large anions such as I\(^-\) tend to induce the polarization of their electronic clouds. This polarization may exert a potent effect on electronic states in alkali iodides and bromides. In the present DV-X\(\alpha\) method, such an effect is implicitly covered, leading to the computed results compatible with this effect: The above calculation has ignored the displacement of ions by the formation of anion defects. However, such a lattice relaxation can affect the electronic state of F-centers. The lattice relaxation will be discussed afterwards.

To understand the interaction between an F-center and surrounding ions, we examine atomic orbital components in the \(a_{1g}\) (F-center state) which can be estimated from the Mulliken population analysis. Figure 2-6 shows the components of the atomic orbitals of surrounding ions in the \(a_{1g}\) state. As the atomic number of anion increases (or that of cation decreases), the component \(A_{1st}\) of the 1st neighbors' orbitals in the \(a_{1g}\) is decreased, while that of 2nd neighbors' atomic orbitals \(A_{2nd}\) increased. In the case of the compounds where the cation has much smaller radius than the anion such as LiI and NaI, it is noteworthy that the contribution of 1st neighbor cations to the \(a_{1g}\) decreases to less than 0.5 and the main part of the F-center state arises from the atomic orbitals of outer ions, suggesting large expansion or more delocalization of the \(a_{1g}\) orbital. The
delocalization of the $a_{1g}$ will increase the energy level, because the $a_{1g}$ electron interacts repulsively with the 2nd neighbor anions. In such a case, the $a_{1g}$ can be reconstucted by the inward relaxation of cations toward the center of the defect, as will be discussed in the following sub-section.

![Graph showing the contribution of atomic orbitals of ions around an F-center to the $a_{1g}$ wave function in various alkali halides. $A_{1st}$ and $A_{2nd}$ indicate the admixing ratios of the atomic orbitals of 1st and 2nd neighbor ions in the $a_{1g}$, respectively.]

Fig. 2-6 Contribution of the atomic orbitals of ions around an F-center to the $a_{1g}$ wave function in various alkali halides. $A_{1st}$ and $A_{2nd}$ indicate the admixing ratios of the atomic orbitals of 1st and 2nd neighbor ions in the $a_{1g}$, respectively.
2.3.3 Lattice relaxation effects

When a vacancy is introduced in a crystal, the lattice around the vacancy is generally considered to be distorted. In case of the O$^{2-}$ vacancy in MgO, it has been mentioned that Coulomb potentials of the system act to displace the 1st neighbor Mg$^{2+}$ ions away from the vacancy and 2nd neighbor O$^{2-}$ toward the vacancy [35]. For an F-center in alkali halides, however, surrounding ions must be displaced in the opposite direction because the potentials are changed by the presence of an electron trapped in the defect. In order to ascertain such displacement, we calculate the level structure, changing the position of the 1st neighbor cations but keeping the $Oh$ symmetry, and estimate the change in the absorption energy $E_a$ due to the lattice relaxation.

Figure 2-7 displays the energy change in the $a_{1g}$ and $t_{1u}$ levels of KCl cluster by the relaxation. The figure indicates that the separation between these two levels is increased with increasing the lattice relaxation though both energy levels are lowered.

In NaCl-type alkali halides, the character of bonding is not purely ionic and some amount of covalency is involved, as quantitatively pointed out by Adachi [12]. The bonding nature of a molecular orbital can simply be estimated from the character of its wave function [10]. When a wave function shows relatively large amplitudes at around the midpoint between two nuclei without changing its sign, the orbital is regarded as that of bonding nature which contributes to the covalency. Conversely, the definite change of its sign at around the midpoint indicates that the orbital is of anti-bonding nature. In the $a_{1g}$ state, the orbital
which consists mainly of 4s and 4p atomic orbitals of the 1st neighbor cations is mostly of bonding nature, as is seen from Fig. 2-3(a). By the inward relaxation, the component of the 1st neighbors’ atomic orbitals in the $a_{1g}$ is increased, indicating the contraction of the state. Therefore, the $a_{1g}$ state more strongly exhibits the bonding nature and its energy level is lowered (Fig. 2-7). This suggests that the inward relaxation tightens the trapping of an electron in the F-center. On the other hand, the $t_{1u}$ state consists mainly of K-4s, 4p and 3d orbitals, while it is partly of anti-bonding nature as is seen in Fig. 2-3(b). Consequently, the
energy level of the $t_{1u}$ is not so much lowered compared with the $a_{1g}$ (Fig. 2-7). As a result, the energy difference between the $a_{1g}$ and the $t_{1u}$ levels is increased by the relaxation of the 1st neighbor cations, suggesting the increase of the F-band energy. For example, the experimental value of the absorption peak is about 2.30 eV [30], while the energy ($E_a$) is computed as 1.81 eV for the case without relaxation. When the 1st neighbor cations are displaced inward, the computed value of $E_a$ increases. In the case of the inward relaxation by 10% of the interionic spacing in KCl, the value computed better fits in with the experimental data.

We have carried out similar calculations taking the inward displacement of the cations, so that the absorption energies calculated coincide with the experimental values [3,18] for all other alkali halides. Table 2-2 lists the degrees of the relaxation of the 1st neighbor cations around F-centers in various alkali halides thus obtained. In this table, fluorides indicate small relaxation, while iodides large. Such tendency can be imagined from the computed results shown in Fig. 2-5. Although magnitudes of relaxation for iodides are estimated to be enormous, the inward relaxation is reasonable for electrically neutral F-centers, where only one electron is present instead of an anion. I- ions have a larger ionic radius than other alkali and halogen ions, and it is possible that large displacement of nearest neighbors around I-vacancies is needed in iodides. In the above calculation, we only allowed the displacement of the 1st neighbor cations around an F-center. The displacement of outer ions may not much affect the F-center state, because the wave function of the $a_{1g}$ is contracted by the relaxation of the 1st neighbor cations.
Table 2-2 Atomic relaxation of the 1st neighbor cations around an F-center (%). Values are estimated from the fitting of computed absorption energies with experimental data. The values listed here correspond to the ratios of their displacement to interatomic spacing of defect-free crystals. The computation allowed only displacement of 1st neighbors.

<table>
<thead>
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<th>(%)</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
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<tbody>
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<td>9.5</td>
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</tr>
</tbody>
</table>
§2.4 Concluding Remarks

We have performed the DV-Xα cluster model calculation for the electronic state of F-centers in NaCl-type alkali halides. The transition energy for photo-absorption by F-centers was calculated on the basis of the Slater's transition state concept. The results obtained are summarized as follows:

(1) The F-center state $a_1^g$ appears within the energy gap between valence and conduction bands. The $a_1^g$ state consists mainly of $s$ and $p$ atomic orbitals of the nearest neighbor cations and is of bonding nature. By the introduction of an anion vacancy, the potential gradient of electric fields toward the center of the defect is induced and causes to lower the energy level of the $a_1^g$.

(2) The optical absorption of F-centers is induced by the transition from the $a_1^g$ to excited states. The photo-absorption of F-centers (F-band) causes by the transition from $a_1^g$ to the $t_1^u$ which is located just above $a_1^g$ energy level. The $t_1^u$ state is composed mainly of $s$, $p$ and $d$ orbitals of a cation, and is in part of anti-bonding nature. The transition from the $a_1^g$ to the $t_1^u$ causes photo-absorption in visible light range of the spectrum. The transition energies ($E_a$) computed for the case without lattice relaxation in compounds with relatively small anions agree well with experimental data, while those in iodides, bromides and some chlorides are much smaller than the observed values.

(3) When the first neighbor cations around an F-center are displaced toward the center of the defect, transition energies $E_a$ computed are increased. When the 1st neighbor cations are displaced, for example, by 10% of the interionic spacing in the case of KCl, the computed value of $E_a$ well fits with the
experimental data. Estimated relaxation of the 1st neighbor cations exhibits relatively small values in fluorides, while it shows larger magnitudes in the compounds with large anions.
CHAPTER 3
ELECTRONIC STATES AND CHEMICAL BONDS OF AN INTERSTITIAL CATION IN IONIC COMPOUNDS AgCl AND NaCl

§3.1 Introduction

Point defects occur naturally in ionic compounds, and produce interesting optical and electrical properties. Several types of point defects are created, but the dominant type of point defects is different in a different compound. AgCl and NaCl are sometimes considered to be similar ionic compounds, since they have the same rock-salt structure. However, intrinsic point defects created in these crystals are different from each other. In NaCl, cation vacancies (Schottky-type) are easy to occur, while interstitial Ag ions (Frenkel-type) abundantly exist in AgCl even at room temperature. These interstitial Ag ions play an important role for the ionic conductivity and the formation of latent image in a photographic process [6-9]. The origin of these intrinsic defects is one of the interesting problems that has been investigated by experiments and theoretical calculations.

According to the experimental photoemission spectroscopy by Tejeda et al. [36] and Bauer et al., [37] the valence band of AgCl is composed of Ag-$4d$ and Cl-$3p$ orbitals, which are well admixed with each other. There have been a number of theoretical calculations on bulk AgCl. Bassani et al. [38] carried out a tight-binding band structure calculation for AgCl. Scop [39] also reported a muffin-tin APW (augmented plane wave) calculation.
Kunz [40] employed a self-consistent Hartree-Fock band calculation, and examined in detail the energies needed for direct and indirect electronic transitions. All these calculations on the valance band structure of AgCl show a fairly good agreement with the experimental photoemission spectra. From these experimental and theoretical studies on the electronic structure of AgCl, it is thought that the chemical bonds of AgCl are not so simple as those of NaCl.

Silver halides exhibit unusual phonon-dispersion curve and cation diffusivity. The origin of these peculiar physical properties has been explained from the viewpoint of Ag-X (X: anion) bonds. In terms of the scale of ionicity by Pauling [41] or Phillips [42], the chemical bond of silver halides partly involves covalency. The partial covalency has been thought to give rise to the unusual cohesive properties of silver halides. Kleppmann and Weber [43] pointed out that Ag ions are less rigid than alkaline ions, and have a strong quadrupolar deformability. Therefore, the AgX lattice is easily distorted, and Ag ions are able to move through the lattice, accompanying lattice distortion. On the other hand, Mayer [44] and Bucher [45] suggested that AgX crystals have strong van der Waals interaction. Bucher has pointed out that the dominance of the van der Waals interaction over short-range electronic repulsion between Ag-X affects the binding energy and elasticity of AgX. Bucher classified crystal structures of AB compounds by the magnitude of the van der Waals interaction.

Among these circumstances, we attempt to investigate the electronic states of AgCl and the chemical bonds around interstitial cations from a simple ionicity-covalency scheme. As
for theoretical calculations of interstitials, Plachenov et al. [46] performed the calculation of an interstitial Ag⁺ in AgCl, using the CNDO (complete neglect of differential overlap) method. They examined the position of local levels of the interstitial within the band gap, and the change of charge density around the interstitial. In the present study, we have carried out a first-principles molecular orbital calculation on an intrinsic interstitial Ag in AgCl crystals, using the DV-Xα cluster method [1,2]. The calculated electronic states are analyzed with special interests on chemical bonds around the interstitial. We have also done the same kind of molecular orbital calculation on NaCl, and made a comparison between AgCl and NaCl.

§3.2 Computational Procedure

In this study, interstitial cations are put into the tetrahedral site of the rock-salt structure. From the correlation factor of the conductivity measurement [47], the diffusion of Ag ions in AgCl crystal is thought to occur by the defect motion of the collinear interstitialcy jump [6]: An interstitial Ag moves by 1/4<111> into a lattice site, and the lattice Ag ion is similarly displaced by 1/4<111> into the adjacent interstitial site. Therefore, an interstitial Ag is generally thought to be located at the tetrahedral site. Figure 3-1 shows structures of model clusters, (a) (MCl₆)⁵⁻ (M=cation, Oh symmetry), (b) (M₅Cl₄)⁺ (Td symmetry) and (c) (M₁₆Cl₁₆). In Fig. 3-1(a), a cation is located at the center of the cluster (normal lattice site), and is surrounded by six nearest neighbor Cl ions. The (M₅Cl₄)⁺ in Fig. 2-1(b) contains an interstitial cation (M(I)) at the center, four cations and four Cl
ions at the adjacent sites. The $(M_{16}Cl_{16})$ in Fig. 2-1(c) comprises 32 ions that are located within the second shell from the interstitial site of the rock-salt structure. For the calculation of a cluster with an interstitial cation, the interstitial is put into the center of the $(M_{16}Cl_{16})$, and the cluster is indicated as $(M_{17}Cl_{16})^{+}$. The interatomic distances are employed from the experimental data for AgCl and NaCl [29]. No relaxation around an interstitial is included in our calculations.

Fig. 3-1 Structures of the model clusters used in this study; (a) $(MCl_{6})^{5-}$, (b) $(M_{5}Cl_{4})^{+}$ and (c) $(M_{16}Cl_{16})$. Solid circles denote cations $(M)$, and open ones Cl ions. The shaded circle at the center in (c) denotes a position of an interstitial cation.
§3.3 Results and Discussion

3.3.1 Electrostatic potentials of the rock-salt structure

In ionic compounds, electrostatic potentials which originate from arrays of charged atoms are thought to be significant for their electronic structures. Before going to a detailed description of valence band structures of NaCl and AgCl, the effects of the electrostatic potentials are examined.

The electrostatic energy of an electron at any lattice point (normal site) due to all charges except the one at that point is given by

\[ V_m = \pm \frac{\alpha_m e^2}{r_0} \]  

where \( r_0 \) is the nearest neighbor distance and \( \alpha_m \) is a constant. This value is called Madelung constant. \( \alpha_m \) is 1.7475 for the rock-salt lattice and \( V_m \) is \( \pm 8.9 \text{ eV} \) for NaCl (Na-Cl = 2.82 Å) and \( \pm 9.1 \text{ eV} \) for AgCl (Ag-Cl = 2.77 Å). The positive value is the one at the normal cation site, and negative at the normal Cl\(^-\) site. In the vicinity of any normal site, the electrostatic energy of an electron is expressed as

\[ V = V_m + \frac{e^2}{r} \]  

where \( r \) is the distance from the normal site. Figure 3-2 shows the contour map of the electrostatic potentials on the (110) plane in the rock-salt lattice due to monovalent charges. As is seen in Fig.
3-2, the electrostatic energy of an electron at the interstitial site (at the center of the figure) is zero.

Fig. 3-2 Contour map of the electrostatic potentials of an electron on the (110) plane of the rock-salt structure (Unit: e/a, a: lattice parameter). The contour spacing is 0.2. The potential in the shaded area is negative. The M⁺ and X⁻ at the corner of the figure denote the positions of a cation and an anion at the normal site.

In this manner, energy levels of ions in a lattice are subjected to the effect of the electrostatic potentials. Figures 3-3(a) and (b) show level diagrams of an isolated M⁺ (cation), an isolated Cl⁻ and those ions at the normal sites in V_m. When a Na⁺ is present at the normal site of the NaCl lattice, energy levels of the Na⁺ are raised by 8.9 eV, as compared to those of the isolated Na⁺. At the same time, energy levels of the Cl⁻ in V_m are inversely lowered by 8.9 eV. This situation is drawn in Fig. 3-3(a). In Fig. 3-3(b), energy levels of the Ag⁺ and Cl⁻ in V_m are similarly shifted by 9.1 eV, as compared to those of isolated ions. It should be pointed out that
the Ag\(^{+}-4d\) level in \(V_{m}\) is located close in energy to the Cl\(^{-}-3p\) level in \(V_{m}\). The energies of the Ag\(^{+}-4d\) and Cl\(^{-}-3p\) levels in \(V_{m}\) differ only by 1.1 eV.

![Level diagrams](image)

Fig. 3-3 Level diagrams of an isolated M\(^{+}\) (cation), an isolated Cl\(^{-}\), and those at the normal site of the NaCl-type lattice composed of ±1 point charges (\(V_{m}\)). Solid lines denote occupied levels, and broken ones unoccupied.
On the other hand, the Na\textsuperscript{+}-2\textit{p} level in \( V_m \) is located by more than 10 eV below the Cl\textsuperscript{-}-3\textit{s} and -3\textit{p} levels even in \( V_m \). The presence of the Ag\textsuperscript{+}-4\textit{d} level whose energy is close to the Cl\textsuperscript{-}-3\textit{p} may provide a striking contrast between the electronic states of NaCl and AgCl.

The electrostatic energies at the normal sites are locally changed when a monovalent positive charge is present at the interstitial site. The electrostatic energy of an electron at the normal site adjacent to the interstitial site is given by

\[
V = V_m - \frac{e^2}{r_i},
\]

where \( r_i \) is the distance between the normal site and the interstitial site. Then energy levels of ions at the normal site adjacent to the interstitial site are reduced by 5.9 eV for NaCl and 6.0 eV for AgCl, as compared to those without the interstitial positive charge. Figure 3-4 shows level diagrams of cations at the interstitial site (M\textsuperscript{+}(I)), the cation (M\textsuperscript{+}(N)) and the Cl\textsuperscript{-} (Cl\textsuperscript{-}(N)) at the normal sites adjacent to the interstitial site. The energy levels of the M\textsuperscript{+}(I) are lower by 3 eV than those of the M\textsuperscript{+}(N) both in NaCl and AgCl, because of the difference of the electrostatic potentials between the M\textsuperscript{+}(I) and the M\textsuperscript{+}(N). Such a difference of the electrostatic potentials will be significant for interaction of atomic orbitals between Ag\textsuperscript{+} and Cl\textsuperscript{-}, because Ag\textsuperscript{+}-4\textit{d} and Cl\textsuperscript{-}-3\textit{p} orbitals are close in energy to each other, as compared to Na\textsuperscript{+}-2\textit{p} and Cl\textsuperscript{-}-3\textit{s}, 3\textit{p} orbitals.

The Ag\textsuperscript{+}-4\textit{d} orbitals are likely to play an important role for valance band structure of AgCl and for chemical bondings around
an interstitial Ag, although the above calculations do not take account of the interaction between atomic orbitals. Detailed electronic structures of bulk crystals as well as interstitial cations will be shown in the following sections.

Fig. 3-4 Level diagrams of a $M^+$ at the interstitial site ($M^+(I)$), a $M^+$ ($M^+(N)$) and a $Cl^-$ ($Cl^-(N)$) at the normal site adjacent to the interstitial site, when an interstitial cation exists: (a) NaCl and (b) AgCl.
3.3.2 Valence band structure of NaCl and AgCl

The calculated results of valence levels for model clusters representing the bulk crystal and that with an interstitial cation in Figs. 3-1(a) and (c) are shown in Fig. 3-5. The HOMOs are set at zero energy. On the right hand of each figure, the density of states (DOS), which is obtained by the broadening of the discrete MO levels by Gaussian functions of 1.0 eV FWHM, is depicted. Valence levels of the (NaCl₆)⁵⁻ cluster are mainly composed of the Cl-3p orbitals. The Na-3s orbitals have very small contribution to the valence band, and the width of the valence band is considerably small (about 2 eV). These features of the valence band are almost the same as those of the larger (Na₁₆Cl₁₆) cluster in Fig. 3-5(b). On the other hand, valence levels of the (AgCl₆)⁵⁻ cluster (Fig. 3-5(c)) are mainly made up by Ag-4d and Cl-3p orbitals. The filled Ag-4d band is located at the top of the valence band, and interacts with the Cl-3p orbitals. This is because the Ag-4d orbitals are energetically close to the Cl-3p orbitals, and interact strongly with the surrounding ions in the valence band. In the (Ag₁₆Cl₁₆) cluster (Fig. 3-5(d)), the distribution of the Cl-3p orbitals in the valence band is broader, and the Cl-3p orbitals have larger components near the top of the valence band than those of the (AgCl₆)⁵⁻ cluster. The energy gap between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of the (Ag₁₆Cl₁₆) is lower by 22% than that of the (AgCl₆)⁵⁻, although the energy gap of NaCl is reduced by only 8% when the larger cluster is used. Cluster size dependence is thus more significant in AgCl than in NaCl. Since these two compounds have Cl⁻ ions in common, larger spatial
distribution of Ag orbitals compared with Na orbitals should be responsible for the size dependence. These results imply that the electronic structure of AgCl is more complicated than that of simple ionic compounds as NaCl.

Fig. 3-5 MO levels and the density of states calculated for the (MCl₆)⁵⁻ and the (M₁₆Cl₁₆) clusters: (a) (NaCl₆)⁵⁻, (b) (Na₁₆Cl₁₆), (c) (AgCl₆)⁵⁻ and (d) (Ag₁₆Cl₁₆).
Figure 3-6 compares the DOS in the valence band obtained for the \((\text{Ag}_{16}\text{Cl}_{16})\) cluster with the experimental XPS (x-ray photoemission spectrum) of AgCl [36]. The density of valence states in AgCl calculated by Kunz [40] is also displayed. The lower part of the figure shows the LDOS (local density of states) of the four Ag and four Cl ions in the central cubic. The zero binding energy is set at the top of the valence band for comparison. We believe that general features of the experimental XPS are well reproduced by our cluster model calculation. According to the present calculation, the most prominent peak B in the XPS can be ascribed to the Ag-4d orbitals, although the peak B is located at lower binding energy by about 0.5 eV than that of the experimental value. The shoulder B' is not well separated from the peak B in our calculation. The Ag-4d orbitals are well admixed with Cl-3p orbitals at around peaks A and C. As a result, the calculated spectrum shows broad valence band of 5 eV FWHM. This is in good agreement with the experimental spectrum. In our calculation, the Cl-3p orbitals have relatively large components around the peak C. This is contrary to the results in previous reports [38-40] in which the major part of the Cl-3p components was claimed to lie around the peak A.
Fig. 3-6 Comparison of the density of states obtained in this study with the experimental XPS spectrum [36] and the DOS calculated by Kunz [40].
3.3.3 *Electronic states of an interstitial cation*

In order to investigate the electronic structure around an interstitial cation, MO levels of the model cluster shown in Fig. 3-1(b) are calculated. Figure 3-7 shows the valence levels of (a) (Na₅Cl₄)⁺ and (Ag₅Cl₄)⁺. The DOS is also depicted, similar to Fig. 3-5. As stated in §3.3.1, when an interstitial cation is present, the electrostatic potentials are locally changed. This results in the shift of energy levels of both M and Cl. For easy comparison between the two valence band structures, HOMOs are set at zero energy. The width of the valence band of the (Na₅Cl₄)⁺ is slightly larger than that of the (NaCl₆)⁵⁻ shown in Fig. 3-5(a), because of the interaction of atomic orbitals between the Na(I) and its surrounding ions. However, the feature of the valence band in NaCl is not largely changed by the presence of the Na(I). On the other hand, the width of the valence band of the (Ag₅Cl₄)⁺ becomes larger by about 2 eV than that of the (AgCl₆)⁵⁻ in Fig. 3-5(c). Nevertheless, the Ag-4d band at the normal site in the (Ag₅Cl₄)⁺ holds its position and is mainly located at the top of the valence band, as the case without Ag(I). While, the Ag(I)-4d band is situated at the bottom of the valence band. This is because of the difference of the electrostatic potential at the Ag(I) from that at the Ag(N), as shown in Fig. 3-4. The difference of the electrostatic potentials between Na(I) and Na(N) in NaCl is almost the same as in AgCl. However, the Na(I)-2p band is located considerably lower than those of the Cl-3s, -3p band, thus the interaction of Na 2p-Cl 3s, 3p is very small in this case. Consequently, it can be mentioned that the presence of the
interstitial cation in NaCl does not change the valence band structure so much as that in AgCl.

Fig. 3-7 Valence MO levels and the density of states calculated for the (M₅Cl₄)⁺ clusters: (a) (Na₅Cl₄)⁺ and (b) (Ag₅Cl₄)⁺.
In order to examine the change of electronic structures around an interstitial more quantitatively, we used a larger cluster model shown in Fig. 3-1(c). Figure 3-8 shows energy levels for (a) the \((M_{16}Cl_{16})\), (b) the \((M_{17}Cl_{16})^+\) and (c) the \((M_{17}Cl_{16})\) clusters. When an interstitial cation is present (Fig. 3-8(b)), the energy levels shift considerably lower than those of the defect-free cluster (Fig. 3-8(a)). This is due to the presence of a positive effective charge of the interstitial cation. It should be emphasized here that the LUMO \((42a_1)\) of the \((Ag_{17}Cl_{16})^+\) is located near the HOMO of the \((Ag_{16}Cl_{16})\). On the other hand, the LUMO \((22a_1)\) of the \((Na_{17}Cl_{16})^+\) is situated higher by about 3 eV than the HOMO of the defect-free cluster. The reason is that an energy gap between the HOMO and LUMO in AgCl is smaller than that in NaCl. As can be seen in Fig. 3-3, the energy difference between the \(Ag^+\) 5s and the Cl\(^-\) 3p in \(V_m\) of AgCl is considerably smaller than the difference between the \(Na^+\) 3s and the Cl\(^-\) 3p in \(V_m\) of NaCl.

The \(42a_1\) orbital is composed mainly of Ag-5s components, and contains 14% of Ag(I)-5s components. Because of the presence of the Ag(I), the \(42a_1\) level is located close to the HOMO of the defect-free cluster. As a result, it is likely possible that electrons are able to transfer from the defect-free region into the interstitial Ag region. While such electron transfer from the defect-free region into the interstitial Na region is not easy to occur in NaCl. When the calculations are made with an extra electron (Fig. 3-8(c)), the electron occupies the \(22a_1\) of NaCl and the \(42a_1\) of AgCl. At the same time, the shift of energy levels takes place and the levels are recovered, so that the top of the
valence band is close to that of the defect-free clusters both for the case of NaCl and AgCl in Fig. 3-8(a).

Fig. 3-8 MO levels calculated for (a) (M$_{16}$Cl$_{16}$), (b) (M$_{17}$Cl$_{16}$)$^+$ and (c) (M$_{17}$Cl$_{16}$) clusters. Upper figures are for NaCl clusters (M=Na), and lower for AgCl (M=Ag). The 22$\alpha_1$ of NaCl and 42$\alpha_1$ of AgCl in which an electron is present are indicated by arrows.
Next we investigate the charge density and its charge of these clusters. The net charge of each ion in these clusters is plotted in Fig. 3-9. In case of the defect-free cluster (Fig. 3-9(a)), the net charges of Na and Cl at the normal site in NaCl (Na(N) and Cl(N)) are higher (namely more ionic) than those of Ag and Cl at the normal site in AgCl (Ag(N) and Cl(N)). In the cluster with the interstitial (Fig. 3-9(b)), the net charges become smaller. It is noted that the net charge of the Na(I) is almost the same as that of the Na(N). However, the net charge of the Ag(I) is smaller by 30% than that of the Ag(N).

Fig. 3-9 Net charges of ions in the model clusters: (a) (M_{16}Cl_{16}), (b) (M_{17}Cl_{16})^+ and (c) (M_{17}Cl_{16}). Open symbols are those for NaCl clusters, and solid ones for AgCl. Circles, triangles and squares are of a lattice cation, an interstitial cation and a lattice Cl, respectively.
This is due to the orbital interaction between the Ag(I) and its surrounding ions in the valence band, as shown in Fig. 3-7. In addition, when an extra electron is introduced (Fig. 3-9(c)), the net charges of the Na(I) and Ag(I) more decrease, as compared to their net charges in the cluster without the additional electron of Fig. 3-9(b).

Figure 3-10 shows the contour maps of (a) the $22a_1$ in the (Na$_{17}$Cl$_{16}$) and (b) the $42a_1$ in the (Ag$_{17}$Cl$_{16}$) on the (110) plane. The $22a_1$ contains 22% of Na(I)-3s and 32% of Na(N)-3s components. The $42a_1$ contains 12% of Ag(I)-5s and 25% of Ag(N)-5s components. Therefore, when the extra electron occupies these MOs, the electron is shared by the interstitial cation and its surrounding cations at the normal site. As a result, net charges of Na(I) and Ag(I) as well as Na(N) and Ag(N) become lower than the case without the electron.
Fig. 3-10 Contour maps of the wave functions of (a) the $22a_1$ in the (Na$_{17}$Cl$_{16}$) and (b) the $42a_1$ in the (Ag$_{17}$Cl$_{16}$) cluster on the (110) plane.
3.3.4 Chemical bonds around an interstitial Ag in AgCl

As stated in the previous section, it is found that an interstitial Ag (Ag(I)) strongly interacts with its surrounding ions. The net charges of the Ag(I) and its surrounding Ag and Cl become considerably low due to the interaction. In this section, we will examine the change of covalent bonds around the Ag(I). As is seen in Fig. 3-2, the electrostatic potential at the interstitial site is zero. This implies that an interstitial cation does not suffer any electrostatic interaction with the surrounding ions. Therefore, the covalent bonds of an interstitial cation with its surrounding ions should play an essential role in stabilizing the interstitial cation.

The overlapping between atomic orbitals in the valence band of NaCl and AgCl is examined. Figure 3-11 shows the energy distribution of overlap populations between Na and its surrounding ions as well as the LDOS of cations and anions in the central cubic of (a) (Na₁₆Cl₁₆) and (b) (Na₁₇Cl₁₆)⁺ clusters. In case of the defect-free cluster (Fig. 3-11(a)), Cl-3p orbitals have weak bonding interactions with Na-3s orbitals. This indicates that electrons of Cl⁻ slightly transfer to Na⁺, and this is the reason why effective charges of Na and Cl are somewhat reduced from the formal charges, ±1. A small bonding character in the unoccupied band is due to the interaction between Na-3s and Cl-3d orbitals. In the cluster with the Na(I) (Fig. 3-11(b)), the Cl-3p band is split into two parts. This is due to the difference of the interaction among the Na(I), its adjacent Na and Cl. As is seen in the right-hand side of Fig. 3-11(b), bonding components of Na(I)-Cl exist at the lower part of the valence band. Anti-bonding components of
Na(I)-Cl exist, but are much smaller than the bonding components.

Fig. 3-11 Diagrams of overlap populations in the valence band of NaCl clusters: (a) the overlap populations of Na-Cl in the $(Na_{16}Cl_{16})$ cluster, and (b) those of Na(I)-Cl and Na(I)-Na in the $(Na_{17}Cl_{16})^+$. 
In case of the AgCl clusters, the diagrams of overlap populations are indicated in Fig. 3-12. The Ag-4d band has anti-bonding interaction with the Cl-3p band at the upper part of the valence band even in the defect-free cluster (Fig. 3-12(a)). This is due to that electrons of two Ag-4d orbitals (dy-type), which point to six ligand Cl ions under $Oh$ symmetry, have repulsive interaction with the ligand Cl ions. When the Ag(I) is present (Fig. 3-12(b)), it is noteworthy that the Ag(I)-4d band is located at the bottom of the valence band, and has bonding interaction not only with Cl-3p orbitals, but also with 4d orbitals of its surrounding Ag. Such interaction of the Ag(I)-Ag in the valence band is much stronger than that of the Na(I)-Na shown in Fig. 3-11(b). The Ag-4d orbital have a large spatial distribution, thus the Ag(I)-4d orbital strongly interacts with its surrounding Ag-4d and Cl-3p orbitals. However, the anti-bonding interaction of Ag(I)-Ag and Ag(I)-Cl is also present in the upper part of the valence band. The net overlap population between ions is determined by the summation of these bonding and anti-bonding contributions, which is given as a bond overlap population in Fig. 3-13.
Fig. 3-12 Diagrams of overlap populations in the valence band of AgCl clusters: (a) the overlap populations of Ag-Cl in the $(\text{Ag}_{16}\text{Cl}_{16})$ cluster, and (b) those of Ag(I)-Cl and Ag(I)-Ag in the $(\text{Ag}_{17}\text{Cl}_{16})^+$. 
Figure 3-13 shows bond overlap populations (BOPs) between ions in various clusters. Results of the AgCl and NaCl clusters are displayed in I and II, respectively. The BOP is a good measure of the strength of covalent bonds between atoms. The BOP of Ag-Cl ($N_{Ag-Cl}$) is larger than that of Na-Cl ($N_{Na-Cl}$) in the defect-free cluster (Fig. 3-13(a)). In the case of the cluster with the interstitial (Fig. 3-13(b)), the $N_{Na(I)-Cl}$ becomes larger than the $N_{Na-Cl}$ in the defect-free cluster. However, the $N_{Na(I)-Na}$ is small. On the other hand, the $N_{Ag(I)-Cl}$ and $N_{Ag(I)-Ag}$ (Fig. 3-13(b)) are both large, as compared to $N_{Ag-Cl}$. The large $N_{Ag(I)-Ag}$ is due to the strong interaction of the Ag-$4d$ orbitals as described for Fig. 3-12(b). It is likely that such a covalent bond makes the interstitial Ag sufficiently stable in AgCl.

As stated in §3.3.3, when the Ag(I) is present, charge transfer from the defect-free region into the interstitial region is possible to occur in AgCl. In order to investigate such charge transfer effect on the chemical bonds, the BOPs of the $(Ag_{17}Cl_{16})^+$ cluster where one more electron is added to the $(Ag_{17}Cl_{16})^+$ are evaluated and shown in Fig. 3-13(c). It should be noted that the $N_{Ag(I)-Ag}$ increases, while the $N_{Ag(I)-Cl}$ decreases. The extra electron fills the $42a_1$ orbital as shown in Fig. 3-8(c). Since the $42a_1$ orbital has a bonding character of the Ag(I) with its surrounding Ag, and an anti-bonding character with its surrounding Cl, as is seen from Fig. 3-10(b). The electron in the $42a_1$ strengthens the Ag(I)-Ag covalent bond but somewhat weakens the Ag(I)-Cl. Nevertheless, the $N_{Ag(I)-Cl}$ is still larger than the $N_{Ag-Cl}$ in the defect-free cluster.

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The BOPs in NaCl change in the similar manner as in AgCl when the extra electron is present at the $22a_1$ orbital. This is because the character of the $22a_1$ orbital is similar to that of the $42a_1$ orbital in AgCl, as seen in Fig. 3-10. However, the $N_{\text{Na(I)-Cl}}$ is considerably decreased when the extra electron exists, and is even smaller than the $N_{\text{Na-Cl}}$ in the defect-free cluster. Therefore, when we consider an electron transfers into the interstitial Na region, a formation of a strong covalent bond between the Na(I) and its surrounding ions can not be expected as the case of the interstitial Ag in AgCl.

![Diagram](image)

Fig. 3-13 Bond overlap populations (BOPs) in (I) AgCl and (II) NaCl clusters: (a) $(M_{16}\text{Cl}_{16})$, (b) $(M_{17}\text{Cl}_{16})^+$ and (c) $(M_{17}\text{Cl}_{16})$. 

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It is known that interstitial Ag ions are abundant in bulk silver halides, but an interstitial Na ion is not easily created in NaCl. According to our results, there is the striking difference of covalent bonds around the interstitial cation between in NaCl and in AgCl. The interstitial Ag has strong covalent bonds with its surrounding Ag and Cl. Besides, an electron is considered to be easily transferred from the defect-free region into the interstitial region in AgCl. This causes the reinforcement of the covalent bond between the interstitial Ag and the adjacent Ag. Such charge transfer is not expected to occur in NaCl. Even if the charge transfer occurs, the interstitial Na does not form the strong covalent bonds with its surrounding Na as in AgCl. The above argument could be related to the change of chemical bonds around the interstitial Ag during an ordinary photographic process. It is suggested that the interstitial Ag ions trap photoelectrons, then Ag clusters are formed when irradiated by visible light. This is thought to be the origin of latent images in the photographic process. From the present investigation, it can be proposed for the mechanism of photographic phenomena in AgCl that an electron which is excited by a photon is transferred to a region where an interstitial Ag ion exists and is trapped there. The electron trapped by the interstitial Ag ion causes to further strengthen the covalent bond with Ag ions surrounding it, and to form an Ag cluster. This can be a source of the latent image.
§3.4 Concluding Remarks

We have performed the DV-Xα calculations for the electronic states of an interstitial cation in AgCl and NaCl using model clusters. We have paid attention to the chemical bonds around the interstitial, and have examined the origin of the difference of intrinsic defects in these crystals. The results obtained are summarized as follows:

(1) Valence band structure of bulk AgCl is quite different from that of bulk NaCl. Ag-4d orbitals are well admixed with Cl-3p orbitals in the valence band. The calculated DOS in the valence band of AgCl shows a good agreement with the experimental XPS.

(2) When an interstitial Ag (Ag(I)) is present, the Ag(I)-4d band appears at the bottom of the valence band. The Ag(I)-4d band strongly interacts with its surrounding Cl-3p and Ag-4d bands. It is found that an unoccupied orbital (42a1) which contains Ag(I)-5s components is located near the HOMO of the defect-free cluster. As a result, the charge transfer from the defect-free region into the interstitial region can easily occur in AgCl. Such charge transfer is not expected to occur in NaCl because the lowest unoccupied orbital (22a1) is located at much higher energy above the HOMO of the defect-free cluster.

(3) By the interaction of the Ag(I)-4d orbitals with its surrounding Ag and Cl, strong covalent bonds around the Ag(I) are formed. In particular, the covalent bond of Ag(I)-Ag is strong, as compared to that of Na(I)-Na in NaCl. In addition, the covalent bond of Ag(I)-Ag becomes stronger by the charge
transfer into the interstitial region. Such strong interaction between Na(I) and its surrounding ions are not observed in NaCl.
CHAPTER 4
ELECTRONIC MECHANISM IN THE FORMATION OF Ag CLUSTERS IN AgBr AND AgI

§4.1 Introduction
Silver halide crystals (AgX, X:halogen) are commonly used as photographic materials. In AgX, interstitial Ag ions abundantly exist even at room temperature. It is known that they contribute to formation of latent images in a photographic process. Several mechanisms of the photographic process in these materials have been proposed by Gurney-Mott [8], Mitchell [9] and Hamilton [6,7]. Figure 4-1 shows the schematic illustration of the process for the latent-image formation.

Fig. 4-1 Schematic illustration of the process of latent-image formation in silver halide crystals.
The process is fundamentally composed of the following steps: 1) formation of a photoelectron and an electron hole by a photon near visible light region, 2) trapping of the photoelectron by interstitial Ag ions or any lattice singularities, 3) diffusion of interstitial Ag ions to the electron-trapping sites, and 4) nucleation and growth of small Ag clusters after the repetition of the above steps. The presence of interstitial Ag ions and their combination with photoelectrons created by photons near visible light region are thought to be important in photographic phenomena.

In general, photographic materials contain AgCl, AgBr or a mixed crystal of AgBr with a few per cent AgI [6]. In the mixed crystal, iodide ions are reported to be substitutionally soluble into AgBr [48]. AgCl and AgBr crystals are indispensable to photographic processes, since they have good photosensitivity. However, the low temperature AgI phase has been rarely employed as a matrix of any photographic materials. The restrictions for photographic applications of AgI have been considered to be mainly originated from two factors [6]: 1) the insolubility in aqueous systems and the resulting less developability of Ag clusters, and 2) the direct band gap in the electronic structure of AgI.

A number of researchers have studied electronic structures near the top of valence band and the bottom of the conduction band of AgX by theoretical band structure calculations [38,40,49-51]. These studies showed that an indirect band gap is present in AgCl and AgBr, and a direct band gap in AgI. The indirect band gaps of AgCl and AgBr result in a long lifetime of the excited state before recombination of a photoelectron and an electron.
hole. This promotes a probability of combination of a photoelectron with interstitial Ag ions, since interstitial Ag ions exist abundantly in AgCl and AgBr. This is thought to be the mechanism of good photosensitivity. Although interstitial Ag ions are also abundant in AgI, the presence of the direct band gap is disadvantageous to the combination of an interstitial Ag ion with a photoelectron in AgI according to this model. However, light absorption experiments by Maskasky [52] showed that, in AgCl/AgI emulsion grains, light was absorbed mainly by AgI, but latent images were formed in AgCl: Photoelectrons generated in AgI are likely to have a relatively longer lifetime before the recombination with electron holes than can be expected for the system having a direct band gap. They are thought to be transferred from AgI to AgCl under light exposure. Ag interstitials in AgI may temporally trap a photoelectron prior to its recombination with an electron hole, similar to the case of AgCl and AgBr, although the timescale required for the trapping may be less than microsec, that is shorter than the lifetime of the photoelectrons. There might be a greater chance of forming Ag clusters even in AgI than expected from the consideration of its direct band gap. Therefore, the rate-controlling factor for the formation of Ag clusters cannot be simply the lifetime of photoelectrons but the stability of Ag clusters under the light exposure. From this viewpoint, we attempt to obtain physical insight into the difference of Ag-cluster formation between AgI and other AgX, on the basis of theoretical analyses of the chemical bonding state of an electron-trapping interstitial Ag ion in these compounds.
In the formation of Ag clusters, the strength of chemical bonds between Ag ions in the clusters is significant. Electronic states of bare Ag clusters were calculated by Baetzold [53] by means of a complete neglect of differential overlap (CNDO) method. He examined ionization potential and binding energy of Ag clusters. In his study, however, the geometry of AgX substrate around an interstitial Ag ion was not taken into account. Plachenov et al. [46] investigated the electronic structure of aggregating interstitial Ag ions in AgCl, using a CNDO method. They paid attention to the energy of interstitial levels in the band gap. In chapter 3, it was found that an interstitial Ag ion has strong covalent bonds with its adjacent Ag ions, because of the presence of a defect-induced level. However, theoretical calculations on an interstitial Ag ion in AgI have been little performed.

We have carried out a first-principles MO calculation on an interstitial Ag ion in AgI, using the discrete variational (DV) Xα method [1,2]. We construct model clusters that include an interstitial Ag, its surrounding Ag and I at normal lattice sites. The electronic states thus obtained are analyzed with special interest on chemical bonds around an interstitial and on a discrete level caused by the presence of the interstitial. A comparison with the case of AgBr is also made, and the difference of Ag-cluster formation between AgBr and AgI is discussed.
§4.2 Computational Procedure

Figure 4-2 shows structures of model clusters for an interstitial Ag (Ag\textsuperscript{i}) in AgBr and AgI. AgBr has the rock-salt structure, and AgI the zinc-blend structure. AgI has several polymorphisms. At temperatures below 147°C, it is polymorphous with the zinc-blend (γ-AgI) and wurtzite structures (β-AgI). In the present study, calculations are made on γ-AgI. This is because the structures of γ-AgI and β-AgI are analogous, and the local atomic structure around an Ag\textsuperscript{i} is almost the same. Therefore, we believe that much insight into the bonding nature of an Ag\textsuperscript{i} in AgI can be obtained from calculations on γ-AgI. The experimental values of the interatomic distances of Ag-Br and Ag-I are employed for AgBr and γ-AgI (Ag-Br=2.89Å, and Ag-I=2.80Å) [29].

Interstitial Ag ions are put into interstitial sites of the rock-salt and zinc-blend structures. The interstitial site of AgBr is the center of a primitive cubic of the rock-salt structure. The AgBr model cluster used in this study (Fig. 4-2(a)) contains 32 ions within the 2nd nearest neighbor (2nd NN) sites from the interstitial site. In the presence of the Ag\textsuperscript{i}+, the cluster is indicated by (Ag\textsubscript{16}Br\textsubscript{16}Ag\textsuperscript{i})\textsuperscript{+} (Td symmetry). The Ag\textsuperscript{i}+ is surrounded by four Ag and four I ions at the normal sites. In the case of AgI, model clusters for two interstitial sites are employed in the present calculations. One site is the interstitial of the Ag sublattice of the zinc-blend structure (Fig. 4-2(b)). Another site is the interstitial of the I sublattice, as shown in Fig. 4-2(c). The interstitial site in Fig. 4-2(b) will be hereafter called to be α-site,
and that in Fig 4-2(c) to be β-site. These clusters comprise 30 ions within the 4th NN sites from the interstitial sites.

![Diagram of model clusters](image)

**Fig. 4-2** Structures of model clusters used in the present study. Solid and open circles denote Ag and halogen ions, respectively. An interstitial Ag (Ag$_i$) indicated by the shaded circle is put at the center of the clusters. On the right hand side of each figure, local structures of ions surrounding the Ag$_i$ are displayed.
The Ag$_{i}^{+}$ at the $\alpha$-site ((Ag$_{14}$I$_{16}$Ag$_{i}$)$^{-}$, $Td$ symmetry) is surrounded by four I ions at the 1st NN sites. Six Ag ions at normal sites are also located at the 2nd NN sites. The distance from the Ag$_{i}^{+}$ to the 2nd NN site is 1.15 times larger than that to the 1st NN site. Inversely, the Ag$_{i}^{+}$ at the $\beta$-site ((Ag$_{16}$I$_{14}$Ag$_{i}$)$^{3+}$, $Td$ symmetry) has four Ag ions at the 1st NN sites, and six I ions at the 2nd NN sites. No relaxation of surrounding ions is included in the present calculations.

As stated in chapter 1, MOs obtained by the calculations are represented by the linear combination of AOs, i.e.,

$$
\phi_{il}(r_k) = \sum_{i} C_{ik} \chi_i(r_k)
$$

By means of Mulliken population analysis [11], the overlap population $Q_{ij}^l$ in eq. (1-8) and the orbital population $Q_{il}^l$ in eq. (1-9) are obtained. In order to evaluate the degree of spatial distribution of the $l$-th MO, the localization index ($L_l$) defined by Ching et al. [54] is obtained by using the orbital population $Q_{il}^l$ as

$$
L_l = \sum_{i} (Q_{il}^l)^2
$$

where

$$
\sum_{i} Q_{il}^l = 1
$$
The $L_l$ has a value between $1/N$ and 1, where $N$ is the total number of AOs in the $l$-th MO. $L_l$ is equal to 1 when the $l$-th MO is perfectly localized, and $1/N$ when perfectly delocalized.

§4.3 Results and Discussion

4.3.1 Valence atomic levels in AgBr and AgI

AgBr and AgI are sometimes considered to be ionic compounds. Arrangement of charged atoms in ionic compounds yields electrostatic potentials, which are thought to significantly affect electronic structures of AgBr and AgI. We first investigate valence level structures of AgBr and AgI, assuming that they are simple ionic compounds constructed by Ag+, Br- and I- ions. Such investigation by a simple ionic model will be helpful in understanding the primary feature of valence structures of AgBr and AgI clusters.

The electrostatic energy of an electron, $V$, at any site in a lattice due to all surrounding charges is

$$V = - \sum_j \frac{Z_j e}{r_j} ,$$

(4-4)

where $r_j$ is the distance to the $j$-th ion owning the $Z_j e$ charge. When an electron is present at any normal lattice site, the electrostatic energy due to all monovalent charges except the one at that site is given by

$$V_m = \pm \alpha_m \frac{e^2}{r_0} ,$$

(4-5)
where $r_0$ is the shortest distance between ions of unlike signs, and $\alpha_m$ a numerical constant known as the Madelung constant. For the rock-salt and zinc-blend structures, it has the value, 1.7475 and 1.6381, respectively. Then $V_m$ is $\pm 8.7$ eV for AgBr (Ag-Br=2.89Å), and $\pm 8.4$ eV for AgI (Ag-I=2.80Å). The positive value is the one at any normal cation site, and negative at any normal anion site. On the other hand, when an electron is present at the interstitial site of AgBr (see Fig.4-2(a)), the electrostatic energy at the interstitial site ($V_i$) is evaluated from eq. (4-4) to be zero. In the case of AgI, the $V_i$ at the interstitial $\alpha$-site is +0.6 eV, and that at the interstitial $\beta$-site -0.6 eV.

When a monovalent positive charge is present at the interstitial site, the electrostatic energy at normal sites is locally changed. The electrostatic energy of an electron at the normal site adjacent to the interstitial positive charge is given by

$$V = V_m - \frac{e^2}{r_i}, \quad (4-6)$$

where $r_i$ is the distance between the normal and interstitial sites. Then electrostatic energies of an electron at the adjacent Ag$^+$ and Br$^-$ sites are reduced by 5.8 eV, as compared to those without the interstitial positive charge. In AgI, the electrostatic energy at the 1st NN (nearest neighbor) sites from the interstitial site is lowered by 5.1 eV, and that at the 2nd NN sites by 4.5 eV.

When isolated Ag$^+$, Br$^-$, I$^-$ and AgI$^+$ ions are present in AgBr or AgI, their atomic levels are subjected to $V$, similar to Figs. 3-3 and 3-4. Figure 4-3 indicates level diagrams of these isolated ions in AgBr and AgI lattices. It should be noted on the left side of
each diagram that the Ag\(^{+-}\)-4d level is located in energy close to the Br\(-\)-4p and I\(-\)-5p levels. The energy difference between the Ag\(^{+-}\)-4d and Br\(-\)-4p levels is 2.6 eV (Fig. 4-3(a)), while that between the Ag\(^{+-}\)-4d and I\(-\)-5p levels is 1.7 eV for the \(\alpha\)-site, and 2.9 eV for the \(\beta\)-site (Figs. 4-3(b) and (c)). These valence structures are very different from those of alkali halide crystals, where occupied \(d\)-level of a cation is not present (see chapter 3).

In addition, the interstitial Ag\(^{+-}\)-4d level is located lower by about 3-4 eV than the Ag\(^{+-}\)-4d at the normal site, in both AgBr and AgI. This is because of the difference of the electrostatic energies between normal and interstitial sites. Although the above results do not take account of interactions between atomic orbitals, such energy difference of the Ag\(^{+-}\)-4d levels between the interstitial and normal sites will result in a difference of orbital interactions between Ag\(^{+}\) and its surrounding ions.

The orbital energies may also be changed by the polarization effect due to the presence of the charged interstitial as discussed by Jost [55]. Lattice relaxation around the interstitial may enhance the polarization [56]. However, as will be shown in §4.3.4, the net charge of the Ag interstitial is much smaller than its formal charge, +1, in the present system. The polarization effect due to the Ag interstitial does not change the qualitative arguments of Fig. 4-3. The polarization effects except for that is caused by the lattice relaxation is automatically included in the self-consistent calculation that will be shown in the following section.

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Fig. 4-3 Level diagrams of an isolated Ag+, an isolated X- (Br or I), and those at the normal site of the lattice composed of monovalent point charges ($V_m$). Solid and broken lines denote occupied and unoccupied levels, respectively.
4.3.2 Electronic structures of an interstitial Ag in AgBr and AgI

In this section, valence states of AgBr and AgI clusters with or without an interstitial Ag⁺ (Ag₁⁺) are investigated. Figure 4-4 displays calculated MO levels and their DOS (density of states) curves for (a) (Ag₁₆Br₁₆) and (Ag₁₄I₁₆)²⁻ clusters, where an Ag⁺ is not included in both cases. In the level diagrams, HOMOs (highest occupied molecular orbital) are set at zero energy. The DOS curves are obtained by the broadening of discrete MO levels by Gaussian functions of 0.5 eV FWHM.

The upper valence band (UVB) of the AgBr cluster (Fig. 4-4(a)) is constructed by Ag-4d and Br-4p orbitals. Ag-5s and -5p components slightly contribute to the UVB. The Ag-4d and Br-4p orbitals are fulfilled by electrons, and interact strongly with each other. This is because the Ag⁺-4d level is situated in energy close to the Br⁻-4p level. The lower valence band (LVB), which is located by about 9 eV below the UVB, is essentially composed of Br-4s orbitals. The unoccupied levels corresponding to the conduction band are constructed by Ag-5s and -5p orbitals. The energy gap between the HOMO and LUMO (lowest unoccupied molecular orbital) is 3.8 eV.

The valence structure of AgI is similar to that of AgBr. In the AgI cluster (Fig. 4-4(b)), Ag-4d orbitals have strong admixture with I-5p orbitals in the UVB. This is also due to that the Ag⁺-4d level is close to the I⁻-5p level. The Ag-5s and -5p components make a small contribution to the UVB. The LVB, which is located approximately 6 eV lower than the UVB, mainly consists of I-5s orbitals. The unoccupied levels are composed of Ag-5s and -5p
orbitals, and the energy difference between HOMO and LUMO is 3.7 eV.

Fig. 4-4 Valence MO levels and their DOS (density of states) curves of the AgBr and AgI clusters without Ag⁺⁺ : (a) (Ag₁₆Br₁₆) and (b) (Ag₁₄I₁₆)²⁻.

When an Ag⁺⁺ is present in AgBr and AgI clusters, the valence level structures calculated are shown in Fig. 4-5 : (a) is for the (Ag₁₆Br₁₆Ag⁺⁺) cluster, (b) for the (Ag₁₄I₁₆Ag⁺⁺), and (c) for the (Ag₁₆I₁₄Ag⁺⁺)³⁺. As stated in §4.3.1, the electrostatic potential is locally changed by the presence of the Ag⁺⁺. As a result, energy levels of the surrounding ions are shifted lower in energy. For simplicity, however, HOMOs are set at the zero energy in Fig. 4-5. The DOS curves are obtained in the same way as those in Fig. 4-4. In this case, the LDOS (local DOS) of ions neighboring the Ag⁺⁺ is extracted from the total DOS of the clusters : The LDOS
of four Ag and four Br surrounding the Ag$_i^+$ is depicted for AgBr, and that of four 1st NN ions and six 2nd NN ions for AgI clusters.

Fig. 4-5 Valence MO levels and their LDOS curves of the AgBr and AgI clusters with Ag$_i^+$: (a) (Ag$_{16}$Br$_{16}$Ag$_i$)$^+$, (b) (Ag$_{14}$I$_{16}$Ag$_i$)$^+$ and (c) (Ag$_{16}$I$_{14}$Ag$_i$)$^{3+}$. 

(a) AgBr

(b) AgI ($\alpha$-site)

(c) AgI ($\beta$-site)
In the presence of the Ag\textsuperscript{i+} in the AgBr cluster (Fig. 4-5(a)), the Ag\textsubscript{i}-4\textit{d} band is located at the bottom of the UVB. However, the Ag-4\textit{d} band at the normal site is mainly situated in the middle of the UVB, which is identical to the case without the Ag\textsuperscript{i+} (Fig. 4-4(a)). This is due to the difference of electrostatic potentials of Ag between at the normal and interstitial sites. As can be seen in Fig. 4-5(a), the Ag\textsuperscript{i+}-4\textit{d} level is lower by 3 eV than the Ag\textsuperscript{+}-4\textit{d} level at the normal site. The difference between the Ag\textsuperscript{i}-4\textit{d} and Ag-4\textit{d} bands in the (Ag\textsubscript{16}Br\textsubscript{16}Ag\textsuperscript{i})\textsuperscript{+} cluster can be qualitatively explained by the simple ionic model in Fig. 4-3(a). The Ag\textsuperscript{i}-4\textit{d} band is admixed with the Ag-4\textit{d} and Br-4\textit{p} bands. Thereby, the width of the UVB becomes broader than that of the case without the Ag\textsuperscript{i+} in Fig. 4-4(a).

When an Ag\textsuperscript{i+} is present in AgI clusters, the valence structures change analogous to the case of AgBr. Regardless of the occupation of the interstitial \(\alpha\)-site and \(\beta\)-site, the Ag\textsuperscript{i}-4\textit{d} band is mainly located in the lower part of the UVB (Figs. 4-5(b) and (c)). The Ag\textsuperscript{i}-4\textit{d} band is situated lower in energy than the Ag-4\textit{d} band. This is also because of the difference of electrostatic potentials between at the normal and interstitial sites. According to the results in Fig. 4-3(b) and (c), the energy difference between the Ag\textsuperscript{i+}-4\textit{d} and Ag\textsuperscript{+}-4\textit{d} levels is approximately 3-4 eV. As compared to the energy difference, however, the Ag\textsuperscript{i}-4\textit{d} band in Figs. 4-5(b) and (c) is located closer to the Ag-4\textit{d} band. This suggests that the valence band structures of the AgI clusters are difficult to be explained by the simple ionic model as shown in Fig. 4-3(b) and (c). This may be originated from the covalent
interactions among ions. This will be discussed in more detail afterwards.

4.3.3. Electron trapping by an interstitial Ag

In a photographic process, an Ag$_{i}^{+}$ is considered to trap a photoelectron. The electron trapping of the Ag$_{i}^{+}$ is an important step before the formation of Ag clusters, which are an origin of latent images. Therefore, the electronic mechanism in trapping an electron is of great interest.

Figure 4-6 displays the level diagrams of AgBr and AgI clusters without and with the Ag$_{i}^{+}$ : (a) is of the AgBr clusters, (b) of the AgI clusters for the $\alpha$-site, and (c) for the $\beta$-site. The level diagram on the left side in each case is for the cluster without the Ag$_{i}^{+}$, and that in the middle for the cluster with the Ag$_{i}^{+}$. In the presence of the Ag$_{i}^{+}$ in AgBr, the energy levels shift lower than in the case without the Ag$_{i}^{+}$, because the Ag$_{i}$ has a positive effective charge to interact attractively with electrons. The LUMO, 51$\alpha_{1}$, contains 14% of Ag$_{i}$-5s components. We can say that the 51$\alpha_{1}$ level is introduced by the presence of the Ag$_{i}^{+}$. This level can be referred to as an interstitial level. The 51$\alpha_{1}$ level is situated at -2 eV, that is close to the top of the valence band in the (Ag$_{16}$Br$_{16}$) cluster. Therefore, charge transfer to the Ag$_{i}^{+}$ from the perfect AgBr lattice can be easy to take place. When the calculation is made with an extra electron, the level diagram is shown on the right side of Fig. 4-6(a). The extra electron occupies the 51$\alpha_{1}$ level, and the shift of energy levels in the cluster with the Ag$_{i}^{+}$ is recovered. Since the 51$\alpha_{1}$ is generated by the presence of
Ag⁺, the occupation of the extra electron at the 51a₁ corresponds to the situation that the extra electron is trapped by the Ag⁺.

Fig. 4-6 MO levels of (a) the AgBr clusters, (b) the AgI for Ag⁺ at the α-site and (c) at the β-site shown in Fig. 4-2. The MO levels on the left side of each case are the result of the cluster without Ag⁺, and in the middle of with Ag⁺. When an electron is added to the cluster with Ag⁺, the result is displayed on the right side.
In the cases of AgI (Figs. 4-6(b) and (c)), the level structures by the presence of the Ag\textsuperscript{i+} are almost the same as in the case of AgBr. The energy levels with the Ag\textsuperscript{i+} shift lower, and the 64\textit{a}\textsubscript{1} (Fig. 4-6(b)) and 65\textit{a}\textsubscript{1} (Fig. 4-6(c)) exist as the LUMOs. The 64\textit{a}\textsubscript{1} contains 25\% of Ag\textit{i}-5s components and the 65\textit{a}\textsubscript{1} 36\% of Ag\textit{i}-5s, which are also interstitial levels. When an extra electron is added to the cluster with the Ag\textsuperscript{i+}, the extra electron occupies these interstitial levels.

Contour maps of the wave functions of the interstitial levels on the (110) plane of AgBr and AgI are shown in Fig. 4-7. Although these interstitial levels contain some amount of Ag\textit{i}-5s components, the features of the wave functions are different among one another. As can be seen in Fig. 4-7(a), the Ag\textit{i}-5s orbital in the 51\textit{a}\textsubscript{1} overlaps considerably with its adjacent Ag-5s and Br-4p orbitals. The Ag\textit{i}-5s orbital has a bonding interaction with the Ag-5s, and an anti-bonding with the Br-4p. On the other hand, although the Ag\textit{i}-5s orbital in the 64\textit{a}\textsubscript{1} also overlaps with its adjacent I-5p orbital in an anti-bonding manner, the overlap with the neighboring Ag-5s orbital is considerably small (see Fig. 4-7(b)). In the case of the 65\textit{a}\textsubscript{1} (Fig. 4-7(c)), the Ag\textit{i}-5s orbital interacts with its surrounding Ag-5s in a bonding manner, whereas the interaction of the Ag\textit{i}-5s orbital with the I-5p at the 2nd NN sites is of weak anti-bonding character. The magnitude of localization of these orbitals can be quantified by the localization index \( L_l \) [54]. The \( L_l \) values are plotted against the Ag\textit{i}-5s components (\%) at the interstitial orbitals in Fig. 4-8. The \( L_l \) values of the 64\textit{a}\textsubscript{1} and 65\textit{a}\textsubscript{1} in AgI exhibit quite larger ones than that of the 51\textit{a}\textsubscript{1} in AgBr. Since the Ag\textit{i}-5s components in the 64\textit{a}\textsubscript{1}
and 65a₁ orbitals are larger than those of the 51a₁, the 64a₁ and 65a₁ orbitals in AgI are found to be well localized at the Agᵢ. While the 51a₁ orbital is more delocalized, and contributions of atomic orbital components of ions neighboring the Agᵢ are greater. These features of the interstitial orbitals will have a great influence on chemical bonds around the Agᵢ⁺ in trapping an electron.

Fig. 4-7 Contour maps of (a) the 51a₁ in the (Ag₁₆Br₁₆Agᵢ), (b) the 64a₁ in the (Ag₁₄I₁₆Agᵢ)²⁻ and (c) the 65a₁ in the (Ag₁₆I₁₄Agᵢ)²⁺ on the (110) plane. The contour spacing is 0.02.
4.3.4 \textit{Change of ionicity around an interstitial Ag}

When the Ag\textsubscript{i} is present in both AgBr and AgI, the Ag\textsubscript{i}-4d orbitals strongly interact with its neighboring ions. The interstitial levels occupied by an electron appear in the band gap. In these characteristic electronic states by the presence of the Ag\textsubscript{i}, chemical bonds around the Ag\textsubscript{i} will be quantified by the Mulliken population analysis [11].

Net charges of ions ($n_A$) in the AgBr and AgI clusters are plotted in Fig. 4-9. The upper part of Fig. 4-9 shows the results of the AgBr clusters, the middle of the AgI clusters for the $\alpha$-site and the lower of the AgI for the $\beta$-site. In the case of the clusters without the Ag\textsuperscript{i+} (Fig. 4-9(a)), the absolute values of $n_{Ag}$ and $n_{Br}$ in the AgBr cluster are a little larger than those of $n_{Ag}$ and $n_{I}$ in the AgI clusters. When the Ag\textsuperscript{i+} is present (Fig. 4-9(b)), the $n_{Ag}$ and $n_{Br}$ at the normal sites in the AgBr cluster are considerably
lower than those in the case of (a). Such tendency in the AgBr cluster is identical to the cases of the AgI clusters. The $n_{\text{Ag}}$ and $n_{\text{I}}$ at the normal sites become smaller in the presence of the Ag$_i^+$. The net charge of the Ag$_i$ ($n_{\text{Ag}_i}$) is as small as the $n_{\text{Ag}}$ at the normal site. These results indicate that the Ag$_i$ interacts strongly with its surrounding ions both in AgBr and AgI.

As stated in §4.3.3, when the Ag$_i^+$ is present, an electron is able to be trapped at the interstitial levels (Fig. 4-6). By the introduction of an extra electron to the interstitial 51$a_1$ level in AgBr, the $n_{\text{Ag}_i}$ is found to become a little smaller than that in the case of (b). The 51$a_1$ level contains 12% of Ag$_i$-5$s$ components. Therefore, the net charge of the Ag$_i$ is a little reduced due to the occupation of an electron at the 51$a_1$.

When an extra electron is added to the clusters with the Ag$_i^+$ at the $\alpha$-site and $\beta$-site of AgI, the electron occupies the interstitial 64$a_1$ and 65$a_1$ levels, respectively. Then, the $n_{\text{Ag}_i}$ becomes lower than that in the case of (b), in the similar way to the case of AgBr. However, the $n_{\text{Ag}_i}$ at the $\alpha$-site is approximately neutral, and that at the $\beta$-site exhibits a small negative value. This is because the 64$a_1$ contains 22% of Ag$_i$-5$s$ components, and the 65$a_1$ 34% of Ag$_i$-5$s$. By this reason, the $n_{\text{Ag}_i}$ in the AgI clusters decreases more drastically, as compared to the $n_{\text{Ag}_i}$ in AgBr, by the occupation of an electron in the interstitial levels.
Fig. 4-9 Net charges of ions in the AgBr and AgI clusters: (a) is for the cluster without Ag$_i^+$, (b) for with Ag$_i^+$ and (c) for with Ag$_i^+$ and an extra electron. As shown in Fig. 4-7, the extra electron occupies the $51a_1$, $64a_1$ and $65a_1$. 

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4.3.5 Covalency of an interstitial Ag

Since the net charges of ions around the Agi become small, it is expected that the Agi forms covalent bonds with its surrounding ions. In particular, an Agi-Ag covalent bond can be considered to be significant for the formation of Ag clusters. Thus the overlap populations between ions in the valence levels of AgBr and AgI are examined.

Figures 4-10 display diagrams of overlap populations \(Q_{A-B}^l\) for (a) the \((Ag_{16}Br_{16}Ag_i)\), (b) the \((Ag_{14}I_{16}Ag_i)^{2-}\) and (c) \((Ag_{16}I_{14}Ag_i)^{2+}\) clusters, respectively. These clusters include an Agi+ and an extra electron at the interstitial levels. On the right hand of the level diagrams, overlap populations of Ag-X at normal sites surrounding the Agi \(Q_{Ag-X}^l\) (X: Br or I), Agi-Ag \(Q_{Agi-Ag}^l\) and Agi-X \(Q_{Agi-X}^l\) are depicted.

In the UVB of the AgBr cluster (Fig. 4-10(a)), the Agi-4d, Ag-4d and Br-4p bands are admixed with each other. The Ag-4d and Br-4p bands \(Q_{Ag-Br}^l\) have bonding interactions in the lower part of the UVB. Interactions of Ag-5sp components with the Br-4p band show small contribution to the bonding character. Strong anti-bonding interactions are also present at the top of the UVB. The nearly filled Ag-4d and Br-4p orbitals considerably overlap in the anti-bonding manner to bring about repulsive interactions. It can be seen in the \(Q_{Agi-Ag}^l\) and \(Q_{Agi-Br}^l\) that the Agi-4d band, which is located at the bottom of the UVB (Fig. 4-5(a)), shows strong bonding interactions with the Ag-4d and the Br-4p bands. The anti-bonding interactions of Agi-Ag and Agi-Br also exist in the upper part of the UVB.
Fig. 4-10 Diagrams of overlap populations in the UVB and at the interstitial levels for the AgBr and AgI clusters with Ag$_i^+$ and an extra electron. In each case, the overlap populations of Ag-X (X: Br or I) at the normal sites ($Q_{Ag-X}$), of Ag$_i$-Ag ($Q_{Ag$_i$-Ag}$) and of Ag$_i$-X ($Q_{Ag$_i$-X}$) are depicted on the right side of MO levels.
In the AgI clusters (Figs. 4-10(b) and (c)), the Ag-4d band overlaps with the I-5p band in a strong bonding manner at the bottom of the UVB. The Ag-5sp components have bonding interactions with the I-5p band, and contribute to the bonding character at the bottom of the UVB. The weak anti-bonding interactions between the Ag-4d and I-5p bands are also present in the upper part of the UVB.

In the case of the Ag$_i$ at the interstitial $\alpha$-site (Fig. 4-10(b)), the Ag$_i$-4d band overlaps with the I-Sp band at the 1st NN site, in the similar way to the Ag-I at the normal sites. However, the overlap of the Ag$_i$ with the Ag at the 2nd NN site is considerably small. This may be due to that the I ions at the 1st NN sites have a large ionic radius, and the Ag$_i$-4d orbitals are prevented to interact with the Ag-4d orbitals at the 2nd NN sites so much as with the I-5p at the 1st NN sites. In the presence of the Ag$_i$ at the interstitial $\beta$-site (Fig. 4-10(c)), the overlap of the Ag$_i$-4d band with the Ag-4d band at the 1st NN site is larger than the $Q_{Ag_i-Ag}^l$ in Fig. 4-10(b). Instead of the strong interaction of Ag$_i$-Ag, the overlap of the Ag$_i$-4d band with the I-5p band at the 2nd NN site is smaller than the $Q_{Ag_i-I}^l$ in Fig. 4-10(b). The Ag$_i$ in AgI strongly interacts with the 1st NN ions, while the interactions with the 2nd NN ions are weaker. However, the orbital interactions of the Ag$_i$ with ions at the 2nd NN sites as well as with ions at the 1st NN sites are not negligible.

As is seen in Fig. 4-7, the wave functions of the interstitial levels (51a$_1$ in AgBr, 64a$_1$ and 65a$_1$ in AgI) are composed of Ag$_i$-5s, Ag-5s and X-p orbitals (X : anion). At the interstitial levels, the $Q_{Ag_i-X}^l$ and $Q_{Ag-X}^l$ are of anti-bonding character, while the
$Q_{\text{AgI-Ag}}$ of bonding. Such orbital interactions can be seen in Fig. 4-7.

The bond overlap population between ions are obtained by the sum of the bonding and anti-bonding contributions over the occupied levels in Fig. 4-10. The bond overlap populations between ions ($N_{A-B}$) thus evaluated are plotted in Figs. 4-11. In the case of the clusters without the Ag$_i^+$ (Fig. 4-11(a)), the $N_{\text{Ag-I}}$ are about twice as large as the $N_{\text{Ag-Br}}$. The Ag-I covalent bond is found to be much stronger than the Ag-Br. When the Ag$_i^+$ is present (Fig. 4-11(b)), the $N_{\text{AgI-Br}}$ and $N_{\text{AgI-Ag}}$ in the AgBr cluster become larger than the $N_{\text{Ag-Br}}$. This is due to that the Ag$_i$-4$d$ band has strong interactions not only with its surrounding Br-4$p$ band, but also with its surrounding Ag-4$d$ band in the UVB, as shown in Fig. 4-10(a). In the presence of the Ag$_i^+$ at the $\alpha$-site of AgI (in the middle of Fig. 4-11), the $N_{\text{AgI-I}}$ exhibits a large value, because of the strong interactions of the Ag$_i$-4$d$ band with the I-5$p$ band at the 1st NN site (see Fig. 4-10(b)). However, the $N_{\text{AgI-I}}$ is slightly smaller than the $N_{\text{Ag-I}}$. The covalent bond of the Ag$_i$ with Ag at the 2nd NN site ($N_{\text{AgI-Ag}}$) is much smaller than the $N_{\text{Ag-I}}$. On the other hand, the Ag$_i^+$ at the $\beta$-site of AgI (in the lower part of Fig. 4-11) has a stronger covalency with Ag at the 1st NN site ($N_{\text{AgI-Ag}}$) than with I at the 2nd NN site ($N_{\text{AgI-I}}$). However, both $N_{\text{AgI-Ag}}$ and $N_{\text{AgI-I}}$ are much smaller than the $N_{\text{Ag-I}}$. 

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Fig. 4-11 Bond overlap populations of Ag-X (X : Br or I) at the normal sites ($N_{\text{Ag-X}}$), of Agi-Ag ($N_{\text{Agi-Ag}}$) and of Agi-X ($N_{\text{Agi-X}}$): (a) is in the case without Agi$^+$, (b) with Agi$^+$ and (c) with Agi$^+$ and an extra electron.
When an extra electron is introduced to the cluster with the \text{Ag}_{i}^{+} (Fig. 4-11(c)), the covalent nature around the \text{Ag}_{i} is changed. In the case of AgBr, the \textit{N}_{\text{Ag}_{i}-\text{Ag}} increases, while the \textit{N}_{\text{Ag}_{i}-\text{Br}} decreases, as compared to those in the case of (b). The Ag-Br covalent bond (\textit{N}_{\text{Ag}-\text{Br}}) is also lowered. This is due to that the interstitial 51\textit{a}_{1} level is of strong bonding character of the \text{Ag}_{i} with its surrounding Ag, while of strong anti-bonding with its surrounding Br (Fig. 4-10(a)). The \text{Ag}_{i}-\text{Ag} covalent bond is reinforced by the occupation of an electron in the 51\textit{a}_{1} level. It should be noted that the \text{Ag}_{i}-\text{Ag} covalent bond is strongest among all covalent bonds in the case of (c). On the other hand, in the case of the \text{Ag}_{i}^{+} at the \alpha-site of AgI, the \textit{N}_{\text{Ag}_{i}-\text{Ag}} and \textit{N}_{\text{Ag}_{i}-\text{I}} do not change largely by the introduction of an electron to the 64\textit{a}_{1} level. As seen in Fig. 4-7(b), the wave function of the 64\textit{a}_{1} level is localized at the \text{Ag}_{i}, and does not contribute to the reinforcement of the \text{Ag}_{i}-\text{Ag} covalent bond so much as the 51\textit{a}_{1} level in AgBr does. In addition, the \textit{N}_{\text{Ag}-\text{I}} is much larger than the \textit{N}_{\text{Ag}_{i}-\text{Ag}}. This situation is almost the same as the case of the \text{Ag}_{i}^{+} at the \beta-site. The \textit{N}_{\text{Ag}_{i}-\text{Ag}} becomes a little larger than that in the case of (b), because of the bonding interaction of \text{Ag}_{i}-\text{Ag} in the 65\textit{a}_{1} level (Fig. 4-10(c)). However, the \textit{N}_{\text{Ag}_{i}-\text{Ag}} is still small, as compared to the \textit{N}_{\text{Ag}-\text{I}}.

In a photographic process, interstitial Ag ions, which are abundant in bulk silver halide crystals, are thought to trap photoelectrons created by a photon near visible light region. In the sequence of photographic processes, the interstitial Ag ions trapping electrons form Ag clusters, which are considered to be an origin of latent images. The formation of strong covalent
bonds between Ag ions should be important for the agglomeration of Ag ions. The present results on AgBr show strong Ag_i-Ag covalent bonds, which is similar to the case of AgCl in chapter 3. On the other hand, interstitial Ag ions in AgI do not have strong covalent bonds of Ag_i-Ag. The Ag-I covalent bonds at the normal sites are very strong, even when interstitial Ag ions exist. These results suggest the easiness of Ag-cluster formation in AgBr. The above argument might be related to the difference of photosensitivity between AgBr and AgI. The easiness of Ag-cluster formation would be one of factors to promote the photosensitivity, although the photosensitivity of silver halides should be, of course, closely connected with other factors: a lifetime of an electron or an electron hole, the concentration of Ag_i ions and their mobility.
§4.4 Concluding Remarks

We have performed a first principles MO calculation on an interstitial Ag (Ag$_i$) in AgBr and AgI by means of the DV-Xα cluster method. We have examined chemical bonds around the Ag$_i$, which are considered to be crucial for the formation of Ag clusters in a photographic process. The results obtained in the present study are summarized as follows:

(1) In the valence band of AgBr and AgI, the Ag-4d and anion-$p$ band are well admixed with each other. When an Ag$_i^+$ is present, the Ag$_i$-4$d$ band also interacts strongly with its surrounding ions.

(2) By the presence of the Ag$_i^+$, the interstitial levels consisting of Ag$_i$-5$s$ components are created in the band gap. However, the interstitial $51a_1$ orbital in AgBr is relatively delocalized, while the interstitial $64a_1$ and $65a_1$ orbitals are well localized at the Ag$_i^+$.

(3) In consequence of the interactions of the Ag$_i^+$ with the surrounding ions, the net charges of the Ag$_i$ and its surrounding ions are reduced. Covalent interactions of the Ag$_i$ with its surrounding ions are then significant. In AgBr, the Ag$_i$-Ag covalent bond is much stronger than any other bonds around the Ag$_i$. On the other hand, the Ag$_i$-Ag bond is not so strong in AgI. Instead of that, the Ag-I covalent bonds at the normal sites are rather strong, even when the Ag$_i$ is present. Since the formation of strong Ag-Ag bonds is essential for the cluster of Ag atoms, the present results indicate that the clusters can be formed easier in AgBr than in AgI.
CHAPTER 5
FORMATION OF Ag CLUSTERS BY AGGREGATING INTERSTITIAL Ag IONS

§5.1 Introduction

The mechanism of formation of a latent-image Ag-cluster in silver halides (AgX) has been paid attention to, because this is of great importance in the photographic science. The main purpose of this chapter is to make a further discussion about the formation of an Ag cluster in AgX, by using the results obtained in the present study.

In the photographic mechanisms proposed by Gurney-Mott [8], Mitchell [9] and Hamilton [6,7], a number of interstitial Ag ions (Agi) trap photoelectrons created by visible light, and aggregate with one another. As a result, the agglomeration of Ag atoms is formed, which is a latent image in the photographic process. Since their mechanisms are based on the aggregation of Agi ions in AgX, the Agi-Agi bond is important for the formation of Ag clusters. In a practical photographic material of AgX, Ag clusters are formed on the surface or in the bulk, even by small light exposure near visible light region. Ag clusters thus formed are still reduced by inorganic or organic agents, and developed into metallic specks, so that AgX crystals are darkened [6,7].

In order to investigate the electronic structure and the stability of Ag clusters, Baetzold has performed semi-empirical molecular orbital calculations on bare silver atom clusters which are assumed to be formed by the aggregation of Agi ions on the
surface of AgX [53,57]. In his method, however, the geometrical structure around Ag\textsubscript{i} ions in AgX crystals has not been taken into account. In other words, although the formation of Ag clusters occurs in AgX crystals, the effect of the substrate is neglected. Thus, theoretical calculations on the formation of Ag clusters in more realistic systems are required in detailed understanding of the mechanism. The use of cluster-model calculations makes it possible to include rigorously the chemical environment around aggregating Ag\textsubscript{i} ions.

In chapter 4, the chemical bonds around a single Ag\textsubscript{i} in AgBr and AgI were examined. The single Ag\textsubscript{i} in AgBr was found to have strong covalent bonds with its adjacent Ag ions at the normal sites. The Ag\textsubscript{i}-Ag covalent bonds in AgBr were stronger than any other covalent bonds around the Ag\textsubscript{i}. This result indicates that Ag ions at normal sites neighboring the Ag\textsubscript{i} participate in the Ag-cluster formation. On the other hand, the Ag\textsubscript{i}-Ag covalent bonds in AgI were much weaker than the Ag-I covalent bond. Unlike the case of AgBr, Ag ions at normal sites in AgI are not likely to contribute to the Ag-cluster formation.

In this chapter, the situation that several numbers of Ag\textsubscript{i} ions in AgBr and AgI are present close to one another are taken into account, and the interactions between Ag\textsubscript{i} ions in AgBr and AgI are examined. When interstitial Ag ions aggregate, the chemical bonds so as to form an Ag cluster are analyzed.
§5.2 Computational Procedure

For the calculations with several Ag ions, the model clusters shown in Fig. 5-1 are employed for AgBr and AgI. The geometry of these clusters is fundamentally identical to that of Fig. 4-2, but the number of Ag ions is different. In the case of AgBr, the \((\text{Ag}_{16}\text{Br}_{16}\text{Ag}_7)\) cluster contains seven Ag ions, where one of them is present at the central interstitial site of the cluster and the remaining six Ag ions are located at the interstitial sites neighboring the central interstitial site. On the other hand, the \((\text{Ag}_{14}\text{I}_{16}\text{Ag}_{5})^{2-}\) cluster includes five Ag ions, in which an Ag ion is put at the central interstitial \(\alpha\)-site, and four Ag ions at the neighboring \(\beta\)-sites (see Fig. 4-2). As stated in Fig. 4-6, an electron is able to be transferred from a defect-free region into the interstitial region by the presence of an Ag ion. In this case, in order to take account of such charge-transfer effect, electrons whose number is equal to that of Ag ions are added to the clusters.
Fig. 5-1 Structures of model clusters used in this chapter. Solid and open circles denote Ag and halogen ions, respectively. Interstitial Ag (Ag\textsubscript{i}) ions indicated by the shaded circles are put at the interstitial sites of the clusters. The AgI cluster includes seven Ag\textsubscript{i} ions, and the AgBr cluster five Ag\textsubscript{i} ions. On the right hand side of each figure, local structures of Ag\textsubscript{i} ions are displayed.
§5.3 Results and Discussion

5.3.1 Interstitial levels

Figure 5-2 displays level diagrams of AgBr and AgI clusters without and with Ag\textsubscript{i} ions. These level diagrams are aligned so as to make the HOMOs to be zero. The framework of the valence band structures with several Ag\textsubscript{i} ions is almost the same as that with a single Ag\textsubscript{i} ion, as shown in Fig. 4-5. Ag-4d, Ag\textsubscript{i}-4d and Br-4p bands are admixed with one another in the valence band of AgBr. The valence band of AgI is composed of Ag-4d, Ag\textsubscript{i}-4d and I-5p bands. In each case of AgBr and AgI, the width of the valence band in the presence of Ag\textsubscript{i} ions becomes broader than that without Ag\textsubscript{i} ions, because Ag\textsubscript{i}-4d bands are strongly admixed with Ag-4d, Ag\textsubscript{i}-4d and anion-p bands. On the other hand, two characteristic levels appear within the band gap in both AgBr and AgI. In the case of AgBr (Fig. 5-2(a)), the 62a\textsubscript{1} and 126t\textsubscript{2} levels exist in the band gap. The 62a\textsubscript{1} contain 19.3% of Ag\textsubscript{i}-5sp orbitals and the 126t\textsubscript{2} 16.5% of Ag\textsubscript{i}-5sp. We can say, therefore, that these levels are introduced by the presence of aggregating Ag\textsubscript{i} ions, and the occupation of electrons at these interstitial levels corresponds to the electron trapping of Ag\textsubscript{i} ions. The 126t\textsubscript{2} orbital, which is triply-degenerated and located higher in energy, is occupied by five electrons, and thus unfilled. In the cluster of AgI (Fig. 5-2(b)), the two interstitial levels, 73a\textsubscript{1} and 140t\textsubscript{2}, are present within the band gap, in the similar way to the case of AgBr. The higher 140t\textsubscript{2} orbital is half filled by electrons. The 73a\textsubscript{1} orbital includes 32.2% of Ag\textsubscript{i}-5sp orbitals, and the 140t\textsubscript{2} 36.7% of Ag\textsubscript{i}-5sp.
Fig. 5-2 Level diagrams of the AgBr and AgI clusters without and with AgI ions. Solid lines denote occupied MO levels, while broken lines unoccupied.

Contour maps of the wave functions of the interstitial levels on the (110) plane of AgBr and AgI are shown in Figs. 5-3 and 5-4. As stated above, these orbitals contain some amount of AgI-5s and 5p components. In the 62a1 and 126t2 orbitals of AgBr (Figs. 5-3(a) and (b)), AgI-5sp orbitals have bonding interactions with 5sp orbitals of Ag ions at the normal sites. Interactions of Br-4p orbitals with AgI-5sp orbitals are of anti-bonding character. These
results are identical to the case with a single Ag\(_i\) ion, as shown in Fig. 4-7(a). In this case, 5sp orbitals of an Ag\(_i\) ion also exhibit bonding interactions with those of the adjacent Ag\(_i\) ions.

Fig. 5-3 Contour maps of the wave functions of the 62\(a_1\) and 126\(t_2\) orbitals on the (110) plane of AgBr. The contour spacing is 0.02.

Fig. 5-4 Contour maps of the wave functions of the 73\(a_1\) and 140\(t_2\) orbitals on the (110) plane of AgI. The contour spacing is 0.02.
The features of bonding and anti-bonding interactions between ions in the $73a_{1}$ and $140t_{2}$ orbitals of AgI (Figs. 5-4(a) and (b)) are similar to the $62a_{1}$ and $126t_{2}$ orbitals of AgBr. I-5p orbitals overlap with Agi-5sp and Ag-5sp orbitals in an anti-bonding manner. Interactions of Agi-Agi and Agi-Ag are of bonding character. However, since the Agi ion at the α-site (at the center of these figures) has four Agi ions of the β-site at its nearest neighbor sites, the bonding interactions between Agi ions in AgI are stronger than those in AgBr. The magnitude of overlap between ions will be quantified by the Mulliken population analysis in the following section.

5.3.2 Ionicity around interstitial Ag ions

Figure 5-5 displays values of net charges ($n_{A}$) in the AgBr and AgI clusters. As shown Fig. 4-9, when a single Agi is present in AgBr and AgI, the net charges of ions around the Agi become smaller than those without the Agi. This is due to the occupation of an electron at the interstitial level and the formation of covalent bonds around the Agi ion. In Fig. 5-5, for comparison, the results in the presence of a single Agi in AgBr and AgI (Fig. 4-9) are also plotted. In the AgBr cluster with seven Agi ions, the absolute values of $n_{Ag}$ and $n_{Br}$, which are the ones for Ag and Br ions at the normal sites, become smaller than those with a single Agi. The $n_{Agi}$ as well as the $n_{Ag}$ and $n_{Br}$ is more reduced to approach neutral. It is noteworthy, here, that the aggregation of Agi ions in AgBr gives rise to the considerable reduction of net charges of ions around Agi ions. On the other hand, the $n_{Ag}$ and $n_{I}$ in the AgI cluster with five Agi ions are almost as large as those with a single
Ag$_i$ ion. The $n_{Ag_i}(\alpha)$ and $n_{Ag_i}(\beta)$, which mean the net charges of Ag$_i$ ions at the $\alpha$-site and the $\beta$-site respectively, are still almost neutral. By the aggregation of Ag$_i$ ions, the net charges of ions in AgI are not so largely changed as those in the case of AgBr.

![Graph showing net charges of ions in AgBr and AgI clusters.](image)

Fig. 5-5 Net charges of ions in the AgBr and AgI clusters. In both cases of AgBr and AgI, values of net charges without an Ag$_i$, with a single Ag$_i$ and with aggregating Ag$_i$ ions are indicated.
5.3.3 Covalent bonds in the presence of aggregating interstitial Ag ions

Since the net charges around aggregating Ag ions are considerably reduced, particularly in AgBr, the ions at the adjacent normal sites are not so much subjected to the effect of Madelung potential as those without Ag ions. Therefore, if strong covalent bonds of Ag-Ag or Ag-Agi are formed, such covalent bonds can contribute to the formation of an Ag cluster. In the previous mechanisms of photographic processes, the covalent bond of Ag-Agi has been thought to be significant. Thus, the overlap populations between Ag ions are examined, and the strength of Ag-Agi covalent bonds is investigated in this section.

Figure 5-6 displays diagrams of overlap populations between Ag ions (QAgi-Agi) for (a) the (AgBr16Ag) cluster, and (b) (AgI16Ag)2− cluster. As can be seen in this figure, Ag ions interact with one another both in the valence band and at the interstitial levels. The overlap in the lower part of the valence band of AgBr is of bonding character between Agi-4d bands, while that in the upper part of anti-bonding. The orbital interactions at the 62a1 and 126t2 levels are of bonding character between Ag-5sp orbitals. This can be also seen in Fig. 5-3. Therefore, the interstitial levels are able to reinforce the Ag-Agi covalent bonds.

In the case of AgI (Fig. 5-6(b)), the Ag-4d bands interact with each other, so that the QAgi-Agi curve in the valence band exhibits bonding character in the lower part and anti-bonding in the upper part. On the other hand, the strong bonding characters at the 73a1 and 140t2 levels can be recognized. The framework of orbital
interactions in AgI is quite similar to that in AgBr, although the magnitude of overlap populations at each band is a little different between AgBr and AgI.

Fig. 5-6 Diagrams of overlap populations between Ag\(^{+}\) ions in the valence band and at the interstitial levels: (a) AgBr, and (b) AgI.
As seen in Fig. 5-6, an $\text{Ag}_i$ ion have considerable orbital interactions with adjacent $\text{Ag}_j$ ions in the valence band and at the interstitial levels of both AgBr and AgI. The bond overlap populations between ions ($N_{A-B}$) obtained by the sum of overlap populations over occupied levels in Fig. 5-6 are displayed in Fig. 5-7. In the similar way to Fig. 5-5, the bond overlap populations in the presence of a single $\text{Ag}_i$ ion are also plotted in this figure. In the AgBr cluster, the single $\text{Ag}_i$ ion exhibits a large value of $N_{\text{Ag}_i-\text{Ag}}$, which is the one between the $\text{Ag}_i$ and the $\text{Ag}$ ions at the adjacent normal sites. When seven $\text{Ag}_i$ ions are present in AgBr, the $N_{\text{Ag}_i-\text{Ag}}$ is also quite large, as compared to the $N_{\text{Ag}-\text{Br}}$ and $N_{\text{Ag}_i-\text{Br}}$. The $N_{\text{Ag}-\text{Br}}$ and $N_{\text{Ag}_i-\text{Br}}$ become considerably small. This is because the interstitial levels within the band gap are antibonding ones of Ag-Br and Ag$_i$-Br, as indicated in Fig. 5-3. The $N_{\text{Ag}_i-\text{Ag}}$ is much smaller than the $N_{\text{Ag}_i-\text{Ag}}$. Therefore, $\text{Ag}_i$ ions in AgBr have strong covalent bonds with its surrounding $\text{Ag}$ ions at normal sites, whereas the covalent bonds between $\text{Ag}_i$ ions are not significant.

The $N_{\text{Ag}-\text{I}}$ and $N_{\text{Ag}_i-\text{I}}$ in AgI decrease with the increase of the number of $\text{Ag}_i$ ions, in the similar manner to the case of AgBr. In this case, the $N_{\text{Ag}_i(\alpha)-\text{Ag}_i(\beta)}$ exhibits a relatively large value. This is due to the bonding interactions between $\text{Ag}_i$ ions at the $\alpha$-site and $\beta$-site at the interstitial levels. However, the $N_{\text{Ag}_i(\alpha)-\text{Ag}_i(\beta)}$ is smaller than the $N_{\text{Ag}-\text{I}}$. The $N_{\text{Ag}_i(\alpha)-\text{Ag}}$ and $N_{\text{Ag}_i(\beta)-\text{Ag}}$ are almost the same as those in the presence of each type of a single $\text{Ag}_i$ (Fig. 4-11). Therefore, even when the aggregation of $\text{Ag}_i$ ions takes place in AgI, the covalent bonds of $\text{Ag}_i-\text{Ag}_i$ and $\text{Ag}_i-\text{Ag}$ are
weaker than those of Ag-I at the normal sites, which can not contribute to the agglomeration of Ag ions.

Fig. 5-7 Bond overlap populations between ions in the AgBr and AgI clusters. In both cases of AgBr and AgI, values of bond overlap populations without an Agi, with a single Agi and with aggregating Agi ions are indicated.
Figure 5-8 summarizes the results on the Ag-cluster formation that have been obtained in chapters 4 and 5. In AgBr, the ionic and covalent interactions between Ag and Br ions at normal sites are both much more weakened by the aggregation of Agi ions. Electron-trapping Agi ions are found to have strong covalent bonds with their neighboring Ag ions at the normal sites, whereas the covalent bonds between the Agi ions are very small. This result indicates that the covalent interactions between the Agi and its adjacent Ag ions at the normal sites should be significant for the formation of an Ag cluster in AgBr. In the previous photographic mechanisms, such interactions of the Agi with Ag ions at the normal sites have not been pointed out. Therefore, it is concluded that the aggregation of Agi ions in AgBr promotes the formation of an Ag cluster, and that Ag ions at normal sites significantly participate in the Ag-cluster formation. On the other hand, the covalent bonds of Agi-Ag and Agi-Agi in AgI are found to be weaker than those of Ag-I at normal sites, even when Agi ions aggregate with one another. Although the relatively strong Agi-Agi covalent bonds are formed in AgI unlike the case of AgBr, the formation of an Ag cluster is expected to be prohibited by the strong Ag-I bonds. These results also well explain the difference of photosensitivity between AgBr and AgI, from the viewpoint of the chemical bonding states of interstitial Ag ions in silver halides.
Fig. 5-8 Covalent bonds around $Ag_i$ ions in AgBr and AgI.
§5.4 Concluding Remarks

In this chapter, chemical bonds around aggregating interstitial Ag ions (Ag\textsubscript{i}) in AgBr and AgI have been analyzed. The interactions between Ag\textsubscript{i} ions have been considered to be significant in the previous photographic mechanisms. Therefore, the interactions of Ag\textsubscript{i}-Ag are mainly paid attention to, and the electronic mechanism of the Ag-cluster formation in these crystals are investigated. The results obtained are summarized as follows:

(1) In the presence of several Ag\textsubscript{i} ions in both AgBr and AgI, Ag\textsubscript{i} ions have much orbital interactions with one another. In addition, characteristic interstitial levels composed of Ag\textsubscript{i}-5sp orbitals appear within the band gap. In the interstitial orbitals, Ag\textsubscript{i} ions exhibit bonding interactions with the adjacent Ag\textsubscript{i} ions as well as with Ag ions at the normal sites. Therefore, these interstitial levels have a role of reinforcement of Ag\textsubscript{i}-Ag and Ag\textsubscript{i}-Ag\textsubscript{i} covalent bonds.

(2) Net charges of ions around aggregating Ag\textsubscript{i} ions are considerably reduced. Such tendency is more remarkable in AgBr than in AgI. This is because Ag\textsubscript{i} ions in AgBr have strong covalent interactions with their adjacent Ag ions at the normal sites. At the same time, the Ag\textsubscript{i}-Br and Ag-Br covalent bonds become considerably small due to the presence of interstitial levels in the band gap. The covalent bonds of Ag\textsubscript{i}-Ag\textsubscript{i} in AgBr is not significant. On the other hand, although Ag\textsubscript{i} ions in AgI have relatively strong covalent bonds with their adjacent Ag\textsubscript{i} ions, the Ag\textsubscript{i}-Ag\textsubscript{i} covalent bonds are weaker than the Ag-I bonds. The Ag\textsubscript{i}-Ag covalent bond is not also strong, similar to the case with a single Ag\textsubscript{i} ion. Thus it is expected that Ag clusters are difficult to
be formed in AgI, even when a number of Ag\textsubscript{i} ions aggregate with one another.
CHAPTER 6
SUMMARY AND CONCLUSIONS

In order to investigate intrinsic and extrinsic point defects in ionic crystals, we have carried out first-principles molecular orbital calculations by means of the discrete variational Xα method. We have paid attention to characteristic electronic states due to the presence of the point defects. The spatial distribution of peculiar wave functions and their influence on the chemical bonds around the point defects have been carefully examined. The results obtained are summarized as follows:

(1) In chapter 2, the electronic states of F-centers in alkali halides with the rock-salt structure are investigated. The electronic transition accompanied by optical absorption is examined on the basis of Slater's transition state concept. The photo-absorption energies of F-centers computed for the compounds with relatively small anions agree well with experimental data, but those for iodides and bromides exhibit much lower values than the observed ones. We have also investigated the change in the absorption energy by the atomic displacement. By the inward displacement of 1st neighbor cations, the absorption energies are decreased to approach the experimental values. The relaxation of the 1st neighbors estimated from the computation exhibits fairly small values in fluorides, while large values in iodides and bromides. These results indicate that the photo-absorption energies of F-center reflect a close
relationship between the spatial distribution of vacancy orbitals and the atomic relaxation around F-centers.

(2) Interstitial cationic defects in NaCl and AgCl are focused in chapter 3. We have examined the origin of the difference of intrinsic point defects in these crystals. In AgCl, Ag-4d orbitals are well admixed with Cl-3p orbitals in the valence band, and the electronic structure of AgCl is quite different from that of NaCl. The cation-anion covalent bonds in AgCl are stronger than those in NaCl. In addition, it is found that an interstitial Ag has a considerably strong covalent bonds with its surrounding Ag ions, because of the presence of the interstitial level and the interactions between Ag-4d bands. Such covalent bonds between Ag ions, which are formed in the ionic compound of AgCl, are likely to play an important role for the stabilization of an interstitial Ag in AgCl.

(3) In chapter 4, interstitial Ag ions in AgBr and AgI are examined. These crystals are very important as photographic materials. The origin of the difference of photosensitivity between these crystals is pursued, from the viewpoint of the easiness of Ag-cluster formation. Although these crystals are considered to be ionic compounds, Ag-4d orbitals are well admixed with anion-p orbitals in their valence band. In the presence of an interstitial Ag (Ag\textsubscript{i}), an interstitial level appears within the band gap. The interstitial orbital is found to be more delocalized around the Ag\textsubscript{i} in AgBr than in AgI. As a result, the interstitial level in AgBr reinforces the Ag\textsubscript{i}-Ag covalent bond. The Ag\textsubscript{i}-Ag covalent bond is
stronger than any other bonds around the Ag\textsubscript{i}. On the other hand, the Ag\textsubscript{i}-Ag covalent bond in AgI is much weaker than the Ag-I bond between the normal sites. Since the formation of strong Ag\textsubscript{i}-Ag bond is essential for the agglomeration of Ag atoms, it is expected that an Ag cluster can be formed easier in AgBr than in AgI.

(4) In chapter 5, the mechanism of the Ag-cluster formation in AgBr and AgI is discussed in detail. When Ag\textsubscript{i} ions aggregate with one another in AgBr, the Ag\textsubscript{i}-Ag covalent bond is much stronger than any other bonds around Ag\textsubscript{i} ions, indicating that Ag ions at normal sites participate in the Ag-cluster formation. The Ag\textsubscript{i}-Ag\textsubscript{i} covalent bond suggested by the previous photographic theories is not significant in AgBr. On the other hand, it is found that the Ag\textsubscript{i}-Ag and Ag\textsubscript{i}-Ag\textsubscript{i} covalent bonds in AgI are not strong, so that the easy formation of an Ag cluster can not be expected in AgI, even by the aggregation of Ag\textsubscript{i} ions.
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