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Semiconductor-superionic phase transition in AgI crystals

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The electronic configuration of chemical bonds between ions forming the structure of the AgI superionics existing in three different crystal modifications is discussed α-, β- and γ-phases.On the basis of the formulated schemes of hybridization of ion orbitals, the structural phase transitions $\gamma \to \beta$ and $\beta \to \alpha$ occurring with increasing temperature are considered.It is shown that in the high-temperature superionic α-phase of the AgI crystal in an external electric field, along with an increase in electronic conductivity, hopping conductivity occurs due to a weakening of the coordination bonds between the ions of the substance and the jumps of silver ions along the ion-conducting channels.

Keywords: phase transition, semiconductor, superionics, AgI, hybridization.

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1. Introduction

There is a fairly large number of data in the literature on the crystalline structure, physical properties and phase transformations in superionic crystals and, in particular, in silver halide crystals. They have been lately added with new findings in the research of dielectric spectra of such superionic materials as AgI and Ag_2S that allow to solve the problem of separate control of electronic and ionic conductivity of thin superionic films [1]. However, there is currently no information regarding the electronic configuration of chemical bonds between ions forming the crystalline structure of substances with superionic conductivity. In order to remove this gap, electronic configurations of chemical bonds between ions determining the physical properties of such typical superionic as silver iodide (AgI), which is known [2] to exist in three different modifications such as α-, β- and γ-phases, are subsequently discussed and reviewed herein.

The first stage of the analysis discusses the low-temperature γ-phase. This phase has a lattice with face-centered cubic structure, for which a hybridization scheme of atomic orbitals of silver and iodine ions is formulated to ensure the crystal lattice stability due to σ-bonds between Ag^+ and I^- ions having different energy. The next stage includes the analysis of electronic configurations of Ag^+ and I^- that define the physical properties of β- and α-phases taking into account that the thermal phase transition (PT) from β-phase to α-phase is a semiconductor–superionic transition comparing with the previous by temperature $\gamma \to \beta$ transition, which is the typical first-kind semiconductor–semiconductor PT with lattice symmetry change, but without addition of a new conductivity type as a result of PT. The analysis discusses the hybridization schemes of atomic orbitals for α-, β- and γ-phases formed using the X-ray diffraction analysis data on the phase lattice symmetry. Using the prepared hybridization schemes, physical causes of the following phenomena are discussed on the microlevel:

1) absence of ion-conducting channels in the β-phase after completion of ($\gamma \to \beta$) type semiconductor–semiconductor PT and presence of ion-conducting channels in the α-phase after completion of ($\beta \to \alpha$) type semiconductor–superionic PT;

2) formation of the electronic and ionic types of conductivity of various phases;

3) crystal lattice configuration stability of the α-phase which is maintained during the superionic conductivity process, despite the temperature destabilization of some chemical bonds between silver ions and iodine ions.

2. Electronic configuration of hybrid orbitals of the γ-phase of AgI

According to the X-ray diffraction analysis [3], for AgI at $T = 293\,\text{K}$ (20°C), there is a two-phase composition of the face-centered cubic γ-phase (space group $F43m$, lattice constant $a = 6.495\,\text{Å}$, number of ions in the lattice cell $Z = 4$) and the hexagonal β-phase with wurtzite configuration (space group $P63mc$, lattice constants $a = 4.592\,\text{Å}$, $c = 7.510\,\text{Å}$, $Z = 2$). The γ-phase is the major phase by the taken volume and the β-phase occupies about 2% of the AgI volume. In the γ-phase, atoms are arranged in the centers of faces and in the vertices of a simple cubic lattice. It corresponds to one of the possible closest sphere packing in space. The nearest to each other Ag^+ and I^- form tetrahedra and octahedra composing a quasiregular mosaic system. It is configured of alternating regular octahedra and tetrahedra with ratio 1 : 2. Silver ion positions in the AgI lattice are non-equivalent. Thus, there are two types of

Table 1. Electronic configurations of Ag^+ and I^- ions in γ-phase of AgI (orbitals participating in hybridization are shown in square brackets)

Element No. 47 in the periodic table: Ag (silver); abbreviated designation of configuration: [Kr] $4d^{10}5s^1$					
Atomic orbitals	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2 4p^6 4d^{10}(5)\mathbf{4f^0}(7)$	$\mathbf{5s^1}(\mathbf{1})\mathbf{5p^0}(\mathbf{3})\mathbf{5f^0}(\mathbf{1})$
Number of electrons on the orbital	2	8	18	18	1
Element No. 53 in the periodic table: I (iodine); abbreviated designation of configuration: [Kr] $4d^{10}5s^2(1)5p^5(3)$					
Atomic orbitals	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2\mathbf{4p^6}(\mathbf{3})\mathbf{4d^{10}}(\mathbf{5})$	$\mathbf{5s^2}(\mathbf{1})\mathbf{5p^5}(\mathbf{3})$
Number of electrons on the orbital	2	8	28	18	7

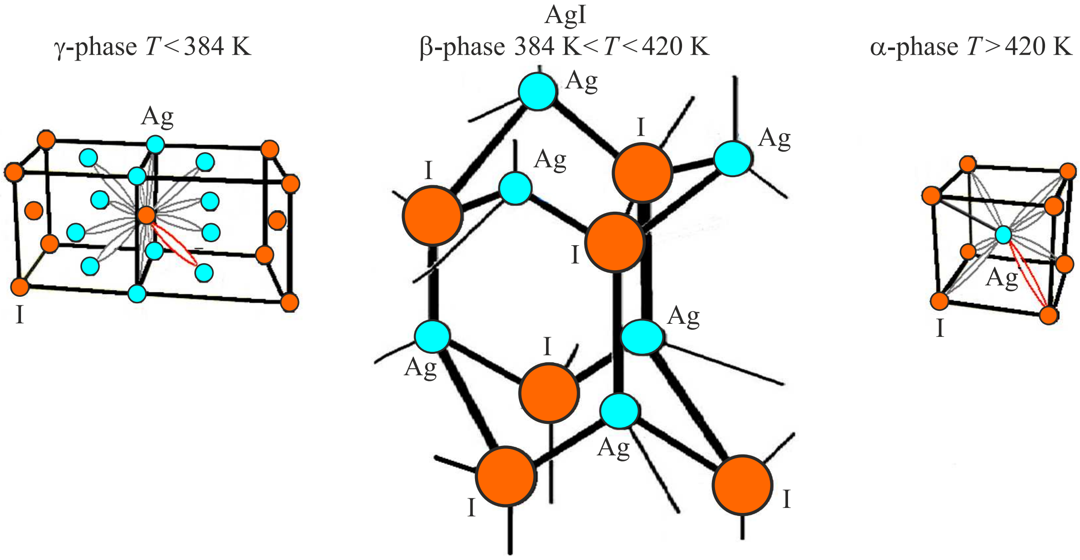

Figure 1. Fragments of the AgI lattice in γ-, β- and α-phases.

positions in the low-temperature γ-phase: tetrahedral and octahedral (see Figure 1).

Formation of crystalline structure of the γ-phase ($T < 384\,K$), β-phase ($384 < T < 420\,K$) and α-phase ($T > 420\,K$) of the AgI lattice will be discussed separately in terms of the valence bond theory. The γ-phase is discussed in this section. Details of the electronic configuration of Ag and I atoms are listed in the tables below for comparison.

With spatial configuration shown in Figure 1, twelve atomic orbitals of Ag atom — $4f^0(7)5s^1(1)5p^0(3)5f^0(1)$ — with a single electron on them (Table 1) participate in the hybridization in the γ-phase. The number of atomic orbitals participating in the total configurations of hybrid orbitals is shown here in brackets. superscripts indicate the number of electrons on the particular atomic orbital used to form the hybrid orbital. For example, designation $4f^0(7)$ shows that 7 electron-free atomic orbitals of the silver atom are used to form the hybrid orbital.

In the γ-phase, twelve atomic orbitals of the I atom having the initial electronic configuration $4p^6(3)4d^{10}(5)5s^2(1)5p^5(3)$ with 23 electrons participate in the hybridization.

Thus, a total of 24 electrons account for twelve hybrid orbitals of silver and iodine ions allowing to form twelve comprehensive σ-bond between Ag^+ and I^- in a face-centered cubic lattice of the γ-phase of AgI. However, attention should be paid to an important fact that eleven from the specified twelve σ-bonds are coordinate σ-bonds, because eleven hybrid orbitals of I^- provide 22 electrons to eleven empty orbitals of Ag^+. Bond energy of coordinate σ-bonds is at least by an order of magnitude lower that the energy of standard σ-bonds [4], during formation of which each of the ions delegates one electron per bond. This provides prerequisites for thermal PT of the material from the γ-phase to β-phase, which is more thermally stable, because the fraction of coordinate σ-bonds with lower strength decreases from 92% (in the γ-phase) to 75% (in the β-phase; see below). This causes a higher temperature of the second PT in AgI, because it is necessary to break thermally a more strong crystalline structure. However, conditions for the occurrence of ion-conducting channels in the β-phase do not occur during PT $\gamma \rightarrow \beta$ due to the features of polytypism of this material, which distinguishes $\gamma \rightarrow \beta$ from the β-phase transition to the superionic α-phase of AgI, where such channels occur. However, the lattice integrity of the α-phase of AgI, despite the formation of ion-conducting channels, is maintained due to the existence of a standard σ-bond, which is by an order of magnitude stronger than the coordinate σ-bond, because each of the ions participating in bond formation delegates one electron to generate this bond [5]. This is a fundamental difference from the coordinate bond formation concept, when one of the ions delegates two electrons to an empty orbital of the second ion. The absence of ion-conducting channels in the β-phase is due to the type ion hybridization in the β-phase lattice of AgI with hexagonal symmetry, for which generation of polytypes with hexagonal symmetry necessary for formation of ion-conducting channels is not possible (Figure 1). Thus, $\gamma \rightarrow \beta$ is caused by the thermal breakdown of primarily eleven coordinate σ-bonds between ions Ag^+ and I^-. This results in the lattice rearrangement from the face-centered cubic to hexagonal structure.

It should be noted that $\gamma \rightarrow \beta$ occurs not only in X-ray diffraction measurements, but also in optical experiments [6]. Thus, during excitation by femtosecond laser pulse of the γ-phase of AgI, a short-lived radiolucent line was detected in the spectral region of exciton absorption of AgI nanocrystals synthesized in the nanoporous silicate glass matrix. The authors of [6] associate the radiolucent line with photoinduced γ-phase $\rightarrow$ β-phase PT, because the nonstable γ-phase has a higher absorption coefficient in the visible spectrum than the βphase and may coexist with it at room temperature.

3. Electronic configuration of hybrid orbitals of the β-phase of AgI

With temperature growth, the β-phase of AgI with hexagonal wurtzite structure $P63mc$ becomes stable at $T = 384\,\mathrm{K}$ (111°C) and occupies 100% of the volume at this temperature. The β-phase has three different types of ion positions: six tetrahedral, twelve trigonal and three octahedral $(6 + 12 + 3 = 21)$ [2]. These three types of positions are crystallographically and energeically non-equivalent. Silver cations occupy these position with various degrees of probability.

In the β-phase of AgI with the hexagonal lattice symmetry, each silver ion and each iodine ion as well have four bonds with the nearest neighbors (Figure 1). For this, Ag^+ delegates, like in the γ-phase, the single electron to four hybrid orbitals $5s^1(1)5p^0(3)$ as shown in Table 2.

I^- delegates seven electrons to four hybrid orbitals $5s^2(1)5p^5(3)$ (Table 2).

Thus, a total of eight electrons account for four hybrid orbitals of each ion of the β-phase, i.e. two electrons per a pair of orbitals, allowing to form complete σ-bonds in the lattice. However, these bonds, like in the γ-phase, are non-equivalent energetically to each other, because seven from eight electrons are delegated to σ-bonds by I^- ions. Six electrons of them are delegated by I^- to the empty orbitals of Ag^+. Hence, three of four σ-bonds in the β-phases are low-strength coordinate bonds and only one of them is a high-strength standard σ-bond. This provides conditions for primary destabilization of the specified coordinate bonds with increasing sample temperature and, thus, for superionic β-phase to α-phase PT.

So, energetic non-equivalence of bonds is defined by electronic configurations of the corresponding hybrid orbitals of silver ions and iodine ions of the β-phase. Three iodine ion orbitals and silver ion orbitals coupled with them are arranged almost in the same hexagon plane (Figure 1) with low angular bond stress according to the Pauling philosophy [7]. The fourth bond interconnects hexagon planes. Therefore, the contrast in the energetic bond „strengths“ ensures thermal breakdown of low-strength bonds at a relatively high temperature $(420\,\mathrm{K})$ and, therefore, superionic $\beta \rightarrow \alpha$ PT. In the α-phase, Ag^+-conducting channels are formed with simultaneous maintenance of crystal lattice integrity due to the existence of high-strength σ-bonds $Ag^+{-}I^-$ and high-strength σ-bonds $I^-{-}I^-$ in the α-phase, whose formation principle is described below.

Thus, coordinate bonds connecting the hexagon planes and coordinate bonds in the hexagon planes are broken first with increasing temperature near the superionic PT point $(T_c = 420\,\mathrm{K})$. This results in crystal structure rearrangement from hexagonal to body-centered cubic structure of the (the β-phase of AgI is transformed into the α-phase of AgI).

Experimentally, completion of the first-kind martensite-type structural $\beta \rightarrow \alpha$ PT [8] is confirmed by X-ray diffraction analysis and is exhibited by a temperature hysteresis loop of AgI film conductivity[9].

With $\beta \rightarrow \alpha$, conductivity increases at least by two orders of magnitude, the hysteresis loop takes a complex form and ionic conductivity appears due to the drift of positively charged silver ions in the external electric field. Occurrence of metallic silver on the negative electrode during DC experiments is also observed. Ionic conductivity of AgI was probably first observed as early as in 1928 in the experiments when a pressed AgI tablet was placed between a silver anode and platinum cathode whose weights were known before [10]. After DC flowing within a fixed period of time, the cathode weight increased and the anode weight decreased by the same value equal to the weight of the metallic silver which had precipitated on the cathode. However, currently there is no consensus regarding the numerical relation of electronic and ionic component

Table 2. Electronic configurations of Ag^+ and I^- ions in β-phase of AgI (orbitals participating in hybridization are shown in square brackets)

Element No. 47 in the periodic table: Ag (silver);
abbreviated designation of configuration: [Kr] $4d^{10}5s^1$

Atomic orbitals	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$3d^{10}$	$4s^2$	$4p^6$	$4d^{10}(5)$	$[5s^1(1)5p^0(3)]$
Number of electrons on the orbital	2	2	6	2	6	10	2	6	10	1

Element No. 53 in the periodic table: I (iodine);
abbreviated designation of configuration: [Kr] $4d^{10}5s^25p^5$

Atomic orbitals	$1s^2$	$2s^22p^6$	$3s^23p^63d^{10}$	$4s^24p^6(3)4d^2(1)4d^8(4)$	$[5s^2(1)5p^5(3)]$
Number of electrons on the orbital	2	8	18	18	7

contributions to conductivity. Therefore, the problem of separation of the contributions made by the electronic and ionic conductors to conductivity is still essential, despite the efforts taken in this area. In particular, the study of dielectric spectra of thin AgI films [1] and „AgI–nanowires–glass“ [11] nanocomposites makes it possible to separate the electronic and ionic contributions to superionic conductivity due to a significant difference in relaxation times of „mobile“ electrons and „slow“ silver ions. Whereby, centers with long relaxation time appear at temperatures close to the PT temperature and are caused by field migration of Ag^+ on the AgI crystallite, when the latter is within the superionic α-phase. However, the question of numerical relation of the electronic and ionic contributions to conductivity is still open [12].

4. Electronic configuration of hybrid orbitals of the α-phase of AgI

In the α-phase, eight orbitals of the Ag atom are involved in the hybridization — $4f^0(7)5s^1(1)$, with a single electron on them, for the electronic configuration see Table 3.

In this case, eight atomic orbitals of the I atom are involved in the hybridization — $4d^8(4)5s^2(1)5p^5(3)$, with 15 electrons on them. The initial electronic configuration is also shown in Figure 3. The proportion of low-energy coordinate σ-bonds is higher here than in the β-phase anf is equal to 87%. Therefore, during transition to the γ-phase, the total stability of the AgI lattice decreases resulting in formation of ion-conducting channels after completion of PT, and the lattice stability is maintained by formation of high-strength I^-–I^- dimers (see below).

This phase becomes stable above 420 K and is superionic as mentioned above. The presence of ionic conductivity together with electronic one is the typical property of the superionic phase: in the α-phase of AgI, ionic conductivity is performed by positively charged silver ions.

Summarizing the above, it may be said that two successive PTs take place in the AgI crystal, when it is heated from room temperature to the temperature above 420 K,: $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$. Each of the three phases (γ, β and α) has energetically unequal chemical σ-bonds: a) high-strength standard σ-bonds, for formation of which ion of each type (Ag^+ type and I^- type) delegates one electron for generation of the σ-bond, and b) low-strength donor-acceptor σ-bonds, for formation of which I^- delegates a pair of its electrons per each empty hybrid orbital of Ag^+. At $T = 384$ K and $T = 420$ K, at which PTs take place, less strong bonds are destabilized and the system changes to a new crystalline modification, where ion attitude is uniquely formed during destabilization of the pre-transition phase. It should be noted that each of three phases has the mentioned above proportion of low-energy coordinate bonds which is different in each phase. This factor defines the AgI crystal capability of performing both PTs at 384 and 420 K, however, without possibility to form ion-conducting channels in the β-phase. According to the crystal lattice symmetry analysis, this is due to the spatial bond configuration. At the same time, according to the detailed lattice symmetry analysis, formation of ion-conducting channels is possible in the α-phase (Figure 2).

It should be noted that the crystal structure of the superionic α-phase has two similar body-centered cubic sublattices inserted one into the other, which consist of Ag^+ and I^- ions, respectively. In the centers of each of the lattice cubes, there are ions with opposite signs: thus, I^- is in the center of the cube with Ag^+ ions arranged in its corners. And vice versa: Ag^+ ions are in the center of the cube with I^- ions arranged in its corners. In this regard, both sublattices are fully equivalent to each other.

In this case, it is correct to raise a question regarding the priority in migration of only one type of ions in the ionic conductivity process of the α-phase, despite full equivalence of Ag^+ and I^- sublattices. First of all, it should be noted that the ionic flow process ensured by the Ag^+ ions is, other things being equal, provided, in addition to coordinate

Table 3. Electronic configurations of Ag^+ and I^- ions in α-phase of AgI (orbitals participating in hybridization are shown in square brackets)

<table>
<tr><td colspan="6">Element No. 47 in the periodic table: Ag (silver);
abbreviated designation of configuration: [Kr] $4d^{10}5s^1$</td></tr>
<tr><td>Atomic orbitals</td><td>$1s^2$</td><td>$2s^22p^6$</td><td>$3s^23p^63d^{10}$</td><td>$4s^24p^64d^{10}(5)[4f^0(7)]$</td><td>$[5s^1(1)]$</td></tr>
<tr><td>Number of electrons on the orbital</td><td>2</td><td>8</td><td>18</td><td>18</td><td>1</td></tr>
<tr><td colspan="6">Element No. 53 in the periodic table: I (iodine);
abbreviated designation of configuration: [Kr] $4d^{10}5s^25p^5$</td></tr>
<tr><td>Atomic orbitals</td><td>$1s^2$</td><td>$2s^22p^6$</td><td>$3s^23p^63d^{10}$</td><td>$4s^24p^6(3)4d^2(1)[4d^8(4)]$</td><td>$[5s^2(1)5p^5(3)]$</td></tr>
<tr><td>Number of electrons on the orbital</td><td>2</td><td>8</td><td>18</td><td>18</td><td>7</td></tr>
</table>

bond destabilization, by the fact that the ionic radius of Ag^+ (0.074 nm) is considerably lower than the ionic radius of I^- (0.133 nm) [13]. The main factor of stability maintenance of the α-phase lattice, despite the destabilization of low-energy coordinate bonds, is the formation of low-energy σ-bonds within $I^- - I^-$ dimers, whose formation is described in detail in the next section.

Movement of migrating silver ions in the superionic crystal during current flow process is complex and combines phonon vibrations of ions in shallow potential energy dips and silver ion hopping in the external electric field from one equilibrium position to another in terms of the type of drift hopping conductivity. I. e. the total conductivity of α-AgI is associated both with hopping and transit mechanisms. In α-AgI, relation of transit time τ_f and „settled life" time of the silver ion in the quantum well τ_s is reported to be of the order of unity [14,15]. It should be taken into account that the change of material crystal structure after thermal destabilization of some chemical bonds during any superionic PT results in the change of the electronic structure, except the ionic structure, and is followed by stepwise growth of the electronic component of conductivity during PT [16].

5. Polytypes of the α-phase of AgI

The fact that one of seven chemical α-AgI bonds requires by an order of magnitude higher energy for breakdown than the remaining six ones plays a fundamentally important role. The experiment shows [15,17] that the α-phase is formed after the semiconductor–semiconductor PT at relatively high temperatures (420 K), when effective thermal generation of free electrons takes place (their concentration increases by two to three orders of magnitude compared with the electron concentration before $\beta \rightarrow \alpha$).

Temperature dependence of conductivity $\sigma(1/T)$ is of thermoactivation type [18]. Near PT, $\sigma(1/T)$, having the logarithmic form of a straight line, changes its slope after PT suggesting that the conductivity activation energy varies during the superionic PT. Thus, in the low-temperature phase, the activation energy is equal to 0.46 eV, while it is considerably lower in the high-temperature phase and in equal to 0.1 eV. The exponential function $\sigma(\omega) = A\omega^2$ of conductivity and frequency ω and the change of exponent s with temperature growth suggest that the hopping conductivity mechanism takes place. In this case, charge carriers (ions, electrons) perform thermally activated hops over potential barriers between the crystal lattice cells.

The foregoing means that a significant number of chemical bonds of the α-phase is destabilized, i. e. a „loose" crystal lattice is formed and „free" silver ions appear which are capable of migrating over the crystal lattice under the external electric field. Probability of defects in the lattice structure increases and, moreover, conditions are provided for polytypism, which is generally typical for silver compounds [19]. Hybridization of atomic orbitals within the polytypes and within the crystalline layers, which separate the polytypes, id different. This issue will be discussed in more detail.

The spatial arrangement of chemical bonds in the lattice is not chaotic, which is due to the general requirement to minimize the thermodynamic potential of the crystal system [20]. Thus, the standard σ-bonds, having by an order of magnitude higher energy compared with the donor-acceptor bonds, are, according to the theory, shorter by 10% than the donor-acceptor bonds [21,22]. The thermodynamic potential minimization condition governs the requirement for such spatial arrangement of high-energy σ-bonds in the adjacent crystal cells, where high-energy σ-bonds are spatially arranged after PT completion at a maximum distance from each other [19]. This is shown in Figure 2. This condition creates a situation, when a particular number of ions along the ion-conducting channel becomes free of high-energy σ-bonds and is kept in its position by only low-energy coordinate (donor-acceptor) bonds. Hence, when polytypes are formed in the AgI crystal, polytype-separating planes of ions weakly bound with neighbors are

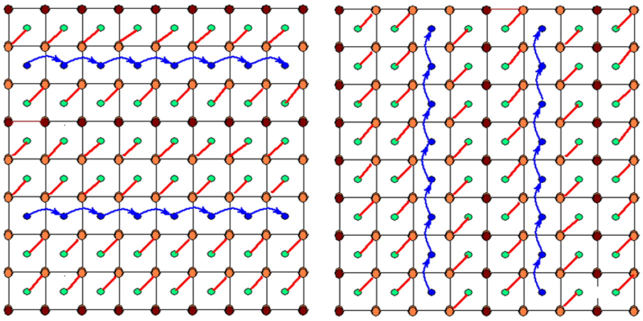

Figure 2. Schematic diagram of polytypes and ion-conducting channels.

formed and provide the possibility of ion migration along such planes at macroscopic distances under the external electric field. Achievement of the temperature at which thermal energy is sufficient for thermal destabilization of the low-energy bonds mentioned above is a prerequisite of migration. In such weakly-bound planes, hybridization of Ag^+ and I^- takes place, other than that described above.

Specifically, I^-, being in the center of the cube with Ag^+ ions arranged in its corners, has eight hybrid orbitals with 16 electrons on them. In this case, hybridization is described by $[4d^{10}(5)5s^2(1)5p^4(2)]\{5p_z^1(1)\}$ configuration, where designations of hybrid orbitals are enclosed in square brackets. A stand-alone $\{5p_z^1(1)\}$ orbital, containing one electron, (enclosed in curly brackets in the configuration designation) calls attention to itself. The AgI crystal lattice, being symmetric relative to the iodine and silver ions, may be also described, as mentioned above, as a body-centered lattice consisting of I^- cubes with Ag^+ iond in the center. In this case, hybridization of atomic orbitals of the Ag atom corresponds to $[4f^0(7)5p_z^0(1)]\{5s^1(1)\}$ configuration, including eight empty orbitals and one stand-alone $\{5s^1(1)\}$ orbital.

Single electrons on $\{5p_z^1(1)\}$ orbitals of I^- and $\{5s^1(1)\}$ orbitals of Ag^+ cannot, according to the theory [21], remain free within the crystal and, using the appropriate σ-bonds, form structures at $T < 420\,K$ consisting of $I^-{-}I^-$ and $Ag^+{-}Ag^+$ dimers similar to $V^{4+}{-}V^{4+}$ dimers formed in the semiconductor phase of VO_2 crystal[23]. It is essential that bond energies of such dimers in AgI are substantially different from each other due to different overlapping of Ag^+ and I^- orbitals in dimers, which, in turn, is defined by the different spatial symmetry of $5s^1(1)$ orbitals (spherical symmetry) and $5p_z^1(1)$ (axial symmetry). Overlapping of $5s$ spheres is several times smaller than that of axial „eights“ $5p_z$ due to the different ionic radii of iodine and silver ions in the AgI lattice [13] and to the different shape of $5s$- and $5p_z$-orbitals. Spherically symmetric $5s$-orbitals of the adjacent silver ions are only overlapped by their single segment zones — sphere volume segments of $5s$-orbitals. At the same time, the „eights“ of $5p_z$ of the iodine ion are overlapped by their lobes arranged in the positive and negative regions of the OZ axis (when zero is positioned in the most narrow place of the „eight“). Taking into account the difference of ionic radii, it may be easily shown that the overlapping region volume of iodine ions in $I^-{-}I^-$ dimers is approximately 7 to 9 times greater than that of the silver ions in similar $Ag^+{-}Ag^+$ dimers. This, according to the theory [4], increases the chemical bond energy of $I^-{-}I^-$ dimers by the same number of times compared with the bond energy of similar $Ag^+{-}Ag^+$ dimers.

The foregoing means that achievement of $T = 420\,K$ of the superionic PT will by followed by the growing probability of hopping of only Ag^+ ions to the adjacent crystal cells due to destabilization within the ion-conducting channels of all eight low-energy coordinate bonds of these ions with crystal lattice and to breakdown of weakly bound $Ag^+{-}Ag^+$ dimers similarly to $V^{4+}{-}V^{4+}$ dimers in VO_2 when the PT temperature is achieved [24]. In addition, drift ionic conductivity occurs in the AgI crystal under the external electric field due to directional hopping of „mobile“ silver ions between crystal cells arranged along the ion-conducting channels parallel to the external electric field vector. At the same time, integrity of $I^-{-}I^-$ dimers, when $T_c = 420\,K$ is achieved, is maintained thanks to their high bond energy, which stabilizes the crystal lattice of the AgI superionic at temperatures higher than the superionic PT temperature $T_c = 420\,K$.

6. Conclusion

Thus, comparison of physical properties of three crystalline modifications of AgI on the basis of the offered hybridization schemes has shown that, despite the differences in the lattice configuration between the described phases, they have common properties playing the fundamentally important role in formation of physical properties of the material. They include: high dark conductivity of both phases and structural phase transformations followed by the change of lattice symmetry and by conductivity growth by several orders. And, crucially, all three AgI phases have chemical bonds whose destabilization energy differs by at least an order of magnitude. The analysis not only clarified the microscopic reasons why formation of conducting channels is impossible after completion of the semiconductor–semiconductor PT ($\gamma \rightarrow \beta$), and why such possibility appears after completion of the semiconductor–superionic PT ($\beta \rightarrow \alpha$). Causes of formation of electronic conductivity of the γ- and β-phases and co-existing ionic conductivity in the α-phase were also found. Finally, the analysis identified the nature of the maintained crystal lattice configuration stability of the α-phase, despite the temperature destabilization of some of its chemical bonds that ensures implementation of superionic conductivity.

It should be noted that the typical feature of AgI is in that all PTs are performed at comparatively high temperatures: $T_c = 384\,K$ (γ-phase $\rightarrow$ β-phase transition) and $T_c = 420\,K$ (β-phase $\rightarrow$ α-phase transition), because the lattice in each of the three phases in low-symmetric state is stabilized by high-energy σ-bonds.

Conflict of interest

The authors declare that they have no conflict of interest.

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