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**Influence of cation substitution on the electron-energy structure of
 $A_7B^{IV}S_5I$ ($A = Cu, Ag$; $B = Si, Ge$)
superionic conductors**

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Abstract

The increased interest to the family of compounds with an argyrodite structure is due to the presence of high ionic conductivity which opens the possibility of using them as the solid electrolytes for a new generation of ionic current sources. An investigation of the electron-energy structure, the features of hybridization of electronic states, and the nature of the chemical bond in the crystalline superionic conductors of $A_7B^{IV}S_5I$ -type is necessary for a deeper understanding of the nature of their high ionic conductivity.

In this paper *ab initio* calculations of the band structure, the total and partial density of states, and the nature of the chemical bonds by means of maps are performed by the method of the density functional theory in the local electron density approximation with allowance for strong correlations in the *d*-shell of the noble metal ion (LDA+*U* method) electron density of $A_7B^{IV}S_5I$ isostructural compounds.

As calculations have shown, all four compounds are direct-gap, and the structure of their energy bands (sequence, relative composition, character of dispersion dependence) is like. The valence band of $A_7B^{IV}S_5I$ consists of four subbands separated by forbidding intervals. The analysis of partial contributions into the density of electronic states allowed to identify the genetic origin of different subbands of the valence band, and also to obtain the formation of a chemical bond in the crystals under study. The most important feature of the electronic spectrum of the $A_7B^{IV}S_5I$ crystals is the presence of an intense peak in the density of states $N(E)$ near the top of the valence band formed by $Cu3d$ ($Ag4d$)-like zone, characteristic of the binary Cu_2S (Ag_2S) compound. The substitution of Cu atoms by Ag atoms in compounds leads to a decrease in the total width of the valence band, expansion of the third and lower bands of valence bands, and to a change in the topology of the two upper bands of the valence band due to the appearance of *pd*-hybridization between noble metal and sulfur atoms. The topology of the edge of the conduction band changes insignificantly.

To describe the chemical bond, maps of the spatial distribution of charge of the valence electrons in the tetrahedra $[Ge(Si)S_4]$, triangles $[Cu(Ag)S_3]$ and bipyramids $[Cu(Ag)_2S_3I_2]$ are plotted. It is visible from the contour maps that the charge density concentrates mainly in the specified structural units, and the contributions of noble metal atoms occupy considerably much larger space region, than the contributions of sulfur, iodine atoms, and especially than silicon (germanium) atoms. The overall nature of the total electron density contours $\rho(\mathbf{r})$ in $A_7B^{IV}S_5I$ crystals shows the ion-covalent bond type. The difference in the chemical nature of the Cu(Ag) and Si(Ge) atoms determines the difference in chemical bonds between Cu(Ag)-S, Cu(Ag)-I and Si(Ge)-S. The Cu(Ag)-S, Cu(Ag)-I bonds are more ionic than the Si(Ge)-S bond, and the Cu(Ag)-S, Cu(Ag)-I bonds are weaker than the Si(Ge)-S.