Electronic Structure and X-Ray Photoelectron Spectra of Some Perovskite Molecular Crystals

A.A. Dotsenko¹, O.L. Shchekina²*, V.V. Korochentsev¹, A.A. Komissarov¹, V.A. Yashin¹, V.I. Vovna¹

¹ Far Eastern Federal University, Vladivostok, Russia
² Far Eastern State Technical Fisheries University, Russia

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It is new study of some molecular crystals with a perovskite structure, whose luminescent, thermochromic, nonlinear optical and dielectric properties provide opportunities for their wide practical application. This paper presents the results of an investigation of the electronic structure and the orbital nature of crystals with the AMX₆ formula (where A = Cs, HGu; M = Te, Sb, Ir, Os, Re, W; X = F, Cl, Br). The electronic structure of crystals with Te and Sb atoms was determined by the method of X-ray photoelectron spectroscopy and quantum-chemical modeling within the framework of the density functional theory. We identified the molecular orbitals which are responsible for covalent metal-halogen binding. Also we found that the transition from the 3a₁u highest occupied molecular orbital to the 4eₗ lowest unoccupied molecular orbital, which corresponds to the states 1T₂ and 3T₁, is responsible for the luminescence of the [MX₆]²⁻ anions.

Keywords: Perovskite crystals, s²-ions, XPS, Density functional theory, Electronic structure, Halides, Luminescence, Molecular orbital.

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1. INTRODUCTION

Molecular crystals with perovskite structure based on s²-ions (In⁺, Tl⁺, Ga⁺, Pb⁺, Bi⁺, Te⁺, As⁺, Sb⁺ and etc) are of great interest in terms of their application for quantum electronics devices and modern energy sources [1]. It is known that these crystals possess luminescent, thermochromic and nonlinear optical as well as dielectric properties, which makes it possible to use them in mesoscopic solar cells, hole conductors, double-perovskite semiconductors, ferroelectric ceramics with perovskite structure [2, 3]. A huge interest in this class of crystals in recent years is due to the discovery of ferroelectric, ferrielectric and ferroelastic phases [4-6].

These crystals have not only covalent bonds but ionic and metallic ones that contribute to the fact that the total electron density becomes more asymmetric and, as a consequence, shifts to the anion-forming agent. In this case, a larger range is observed between the maximum and minimum value of the periodic potential in the crystal field [7]. Binding to cations the perovskites form clusters with tight packing of layers, where some of them demonstrate polymorphism and phase transitions caused by the dynamics of rotation of organic cations. However, luminescent properties are not observed in certain crystals where halogen ligands F, Cl, Br, I are bound to s²-ions or metals (it is known that these properties are mostly determined by metal ions with mercury-like electron configuration ns²). The transitions between sp-excited 3P and s²-ground 1S₀ states are considered responsible for the luminescence process, so luminescence has an intraionic character [8]. An important role in luminescence is also played by the correlation of the Jahn-Teller effect with the spin-orbit interaction, and the presence of an anomalously large Stokes shift, which can reach 20,000 cm⁻¹-30,000 cm⁻¹. The probability of optical transitions in crystals depends mainly on the nearest surroundings of the s²-ion and its structure. In this case, the unshared electron pair, due to the spin-orbit interaction, leads to mixing the electronic transitions of various types, which further complicates their interpretation.

It is necessary to note that the existing luminescence theory based on the terms of atomic ¹S₀ and ³P₁, ³P₂ states is applicable only for metal ions with s²-configuration and for describing the luminescence of metal halide anions such as SbX₆³⁻ and TeX₆²⁻ (X = Cl, Br). This applicability is limited by the fact that the 5s-AOs of the metal are hybridized with the group orbitals of halogens, and the rules for selecting optical transitions and localizing electronic states require the use of descriptions in terms of irreducible representations.

All above mentioned requires for a detailed study of the electronic structure of crystals with the ABX₆ general formula (A = Cs, guanidine, NN-diphenylguanidine; M = Te, Sb, Ir, Os, Re, W; X = F, Cl, Br) in order to determine their physical and chemical properties and sequence of the electronic levels, as well as the definition of the correlation "electronic structure - properties."

2. CALCULATION AND EXPERIMENTAL METHODS

The crystals with Te and Sb atoms studied in this paper were synthesized in the Laboratory of Light-Transforming Materials of the Institute of Chemistry, Far-Eastern Branch of the Russian Academy of Sciences. Synthesis and crystal structure were described in details in the paper [8]. An information about structure of molecular crystals was taken from the paper [9] and Cambridge Structural Data Base [10].
A great contribution to the understanding of the electronic structure of MFs (M = Te, Cr, Mo, W) and identification of the photoelectron spectra was made by calculations [11, 12].

X-ray photoelectron spectra were obtained by us on an Omicron ultrahigh-vacuum photoelectron spectrometer. An X-ray tube with a magnesium anode (MgKα – 1253.6 eV) was used as a source of radiation. The chamber pressure during the experiment did not exceed 9 × 10⁻⁹ mbar. The value of the emission current was I = 13 mA and the anode voltage – U = 10 kV. Sections of the spectra of the characteristic levels of the atoms O1s, C1s, N1s, Cl2p, Br3p were recorded at the transmission energy of the analyzer of 20 eV.

During the registration of spectra the characteristics of the lines did not change. The calibration of the electron binding energy scale was performed based on carbon level C1s. The spectra were processed with the use of Casa XPS software [13]. The test compounds were powders applied to an adhesive substrate.

The spectra were processed by standard procedures. The spectrum background was subtracted by the Shirley method [14]. Spectral smoothing was performed with the use of the Savitzky-Golay digital polynomial filter (SG), a quadratic function with an approximation of interval length of 13 points was chosen as a polynomial approximation in the SG filter. The spectra of outer-shell electrons were interpreted on the basis of calculations of the electronic structures of model compounds and regularities in the X-Ray photoelectron spectra of investigated and related compounds according to the procedure we described in [15, 16].

The calculation of the electronic structure was performed by an ab initio quantum chemical method of DFT with the use of the software systems FireFly and GAMESS-US [17, 18] and a hybrid three-paremeter exchange correlation functional B3LYP [19] with effective core potential of R. Ahirachs for the atoms of tellurium, antimony and cesium [20]. We used the 6-31G, def2-SVP, def2-TZVP basis sets for the calculations [20].

3. RESULTS AND DISCUSSION

3.1 Model Complexes and Electronic Configuration

Figure 1 shows the images of model complexes with the AMXₜ general formula (A = Cs, guanidine, N’N-diphenylguanidine; M = Te, Sb, Ir, Os, Re, W; X = F, Cl, Br).

According to the obtained crystallographic data [9], the complex molecular crystals are anions with the MXₚ general formula (Fig. 1a), where M = Sb, Te; X = Cl, Br; z – is the charge of the anion, which is surrounded by outer-sphere cations of guanidine (Figure 2b), N’N-diphenylguanidine (Figure 2c) and cesium.

The description of the electronic structure and X-Ray photoelectron spectra of the valence band was carried out on the basis of theoretical modeling in the cluster approximation using model compounds with the MXₜ general formula and compounds (Fig. 2) taking into account the maximum number of interactions in real crystals.

According to calculation the electronic configuration of the valence band of octahedral anions is: 1a₂g²1t₁u²1eₓ²2a₁g²2t₁u²1t₂g²2eₓ²3t₁u²1t₄u''1t₅u''3a₁g²4t₁u''.

The shape and symmetry of the main molecular orbitals of octahedral anions are shown in Fig. 3 using the example of [TeCl₆]⁻².

3.2 Electronic Structure of Some Perovskite Fluorides

It was previously believed, that LUMO (lowest unoccupied molecular orbital) in these salts is s-type metal valence orbital (its composition according to calculation: 67 % Se 4s in SeF₆, 67 % Te 5s in TeF₆, 68 % Te 5s in TeF₅ and 63 % Te 5s in OTeF₅), which is antibinding to ligands and corresponding to a stereochemically inactive unshared pair.
The energy of LUMO is extremely sensitive to the lengths of the M-F bonds. Minor changes in distance lead to significant changes in the energy of LUMO. HOMO (highest occupied molecular orbital) in TeF₆, TeF₅, and TeF₄⁻ is the orbital of the fluorine unshared pair. Removal of one fluorine ligand (Fig. 4) leads to the re-hybridization of the 3a₁g orbital in TeF₆ to the 6α orbital (unshared pair) in TeF₅, causing the increase of the length of all Te-F bonds to 2.10 Å. SCF (self-consistent field) calculation demonstrated that in contrast to the heavier halides [TeX₆]²⁻ (where X = Cl, Br), the electron pair 5s² in [TeF₆]²⁻ and [SeF₆]²⁻ can not be easily adapted in a stable octahedral O₆ or non-octahedral C₃v configuration, and attempts to synthesize salts of A₂[TeF₆] or A₂[SeF₆] types must take into account that these salts can only be stable in solution with a reducing medium and at a low temperature.

![Diagram of TeF₆, OTeF₅, TeF₄⁻](image)

Fig. 4 – Correlation diagram for TeF₆, OTeF₅, TeF₄⁻

Figure 5 shows the one-electron energy of the (Fₓ)⁶⁺-cluster with the 'tie'-MO of the HOMO 1αₕ to the corresponding level in the molecule MoF₆. The energy of MOs of isoelectronic molecules of the TeF₆ type is determined mainly by three factors: a) the energy of atomic orbitals; b) the degree of delocalization of ligand MOs to a central atom; c) the efficiency of the interaction of electron pairs of neighboring halogen atoms, which depends on the interatomic distances.

Covalent bonding in hexahalides of p-elements is realized by the interaction of the ns- and np-orbitals of the central atom with the group 2pₓ⁻orbitals (1αₕ)(σ) and the 1αₗg(σ). The calculation shows the stabilizing of the binding orbitals 2αₗg and 2αₖg relative to the cluster levels on 5.2 and 3.4 eV. The energy of these two MOs strictly depends on the energy of the 5s and 5p atomic orbitals of tellurium. The correlation diagram (Fig. 5) shows a slight (<1 eV) covalent stabilization of only 2αₗg-MO where the contribution of Te d-AO is 10% according to calculation.

![Diagram of TeF₆, MoF₆ orbitals](image)

Fig. 5 – Correlation diagram of TeF₆ and MoF₆ orbital energies and (Fₓ)⁶⁺ group orbital energies

When a p-element is replaced by a d-metal, the sequence and binding character of the MOs is significantly altered. The orbitals 1αₕ(σ) and 1αₗg(σ) become practically non-bonding, since their energies are close to the energies of the group orbitals in the cluster, and the orbitals 2αₗg and 1αₖg lower the energy by 4.0 and 1.4 eV as a result of mixing with Mo 4d-AO. Fluorine 2p – orbitals in octahedral structure are transformed according to irreducible representations 1αₕ, 2αₗg, 1αₖg, 2αₗg, and 2αₖg – to irreducible representations 1αₕ, 2αₗg, and 1αₖg are F–F bonding. Metal atom contributes sufficiently to MOs 2αₗg and 2αₖg, 2αₗg, and 2αₖg. Fluorine 2s-orbitals make remarkable contribution to inner levels 1αₕ, 1αₙ, and 1αₗ.

3.3 XPS Spectra Some Perovskite Fluorides

Six and seven bands in the photoelectron spectra of MF₆ (M = W, Ir, Os, Re) (Fig. 6) are observed respectively in the ionization range of seven p-type orbitals (15-20 eV).
The magnitude of the splitting of the $g$-levels is directly proportional to the contribution of the $p$- and $d$-states of the metal, since the splitting of the F2p-orbitals can be neglected. And the splitting of the $t_{2g}^{-}$ level can be caused by the $d$-state, and the $t_{2u}$-level – by the $p$-state of the metal. For WF$_{6}$, the splitting values (eV) are $1t_{2u} - 0.15, 2t_{2u} - 0.3, 3t_{2u} - 0.2$.

The relatively large splitting of the ligand levels of $t_{2u}$ symmetry indicates the contribution of the occupied 5p metal orbital, for which the magnitude of the spin-orbital splitting reaches 10 eV. Consequently, the bands in the WF$_{6}$ spectrum at 16.83 and 17.22 eV, which have close Frank-Condon contours and the integral ratio of 2:1, in accordance with the calculation can be attributed to the sublevels $\gamma u$ and $\gamma u$ of orbital 2$t_{2u}$.

The contribution of the 5p-orbital is estimated at 4 % from the splitting value (0.41 eV). In the band related to 1$t_{2g}$-orbital of WF$_{6}$ we can see two vibrational progressions of valence vibrations $v_1$, which confirms the splitting of the binding 1$t_{2g}$-orbital due to Md-F2p mixing (Fig. 7).

Obviously, for the MoF$_{6}$ molecule there is a contribution of the atomic 4$p$ and 4$d$ orbitals to the MOs of $t_{2u}$ and 2$t_{2g}$-symmetry, respectively. In the molecules of following the tungsten elements – Re, Os and Ir – the anti-bonding 2$t_{2g}$-orbital is occupied.

The single 2$t_{2g}$ electron in ReF$_{6}$ gives a weak band at 11.43 eV. The removal of one of the two 2$t_{2g}$-electrons in OsF$_{6}$ leads to the G2s and E2s states (12.50 and 13.10 eV) with a relative population of ~ 6:1. The 2$t_{2g}$ configuration in the IrF$_{6}^{+}$ ion gives the $9T_{1g}$ state as the lowest that is split due to the spin-orbital interaction to states:

$$A_{1g} + E_g + T_{1g} + T_{2g},$$

which follow from the direct multiplication of irreducible representations of the spatial ($T_d$) and spin ($T_c$) functions in the double point symmetry group $Oh$. Four bands of different intensities correspond to these states in the photoelectron spectrum of IrF$_{6}$ in the range of 13.3-13.9 eV.

![Photoelectron spectra of MF$_{6}$](image)

According to the calculations (Table 1) the second band in the spectra of both complexes belongs to the levels 1$t_{2u}$ and 3$t_{1u}$. In WF$_{6}$ the additional eighth ionization potential refers to the 2$t_{1u}$-level due to the close to the observed spin-orbital splitting obtained. When the spin-orbital interaction is taken into account the triply degenerate MOs split into two sublevels:

$$1t_{1g} \rightarrow \gamma g + \gamma g; 1t_{1g} \rightarrow \gamma u + \gamma u;$$

$$1t_{2g} \rightarrow \gamma g + \gamma g; 1t_{2g} \rightarrow \gamma u + \gamma u.$$

### Table 1 – Vertical ionization potentials (eV) for hexafluorides of Mo, W, Re, Os, Ir

<table>
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<tr>
<th>MO</th>
<th>MoF$_{6}$</th>
<th>WF$_{6}$</th>
<th>ReF$_{6}$</th>
<th>OsF$_{6}$</th>
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<td>$I_b$</td>
<td>$I_a$</td>
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<tr>
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<td>15.15</td>
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<td>16.55</td>
<td>16.83</td>
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<td>17.62</td>
<td>18.43</td>
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</tr>
<tr>
<td>1$t_{2g}$</td>
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<td>18.9</td>
</tr>
<tr>
<td>2$e_{g}$</td>
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<td>19.08</td>
<td>19.28</td>
<td>19.36</td>
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The energy splitting of the $E_g$ and $T_{2g}$ states (degenerated in the octahedron) indicates a distortion of the octahedron. Unpaired $2t_{2g}$-electrons split ligand levels due to spin polarization. The number of final states for an ion with two unfilled shells can be easily determined from group-theoretical representations.

For example when $1t_{2g}$-electron is removed in ReF$_6$ the configuration ...$1t_{1g}^22t_{2g}^1$ leads to ten states if we take into account only the lower state $G_{2g}$ from the spin-orbital doublet $2^2T_{2g} \rightarrow G_{2g} + E_{2g}$:

$$G_{2g}(2^2T_{1g} \rightarrow G_{2g} + E_{1g}) = A_{1g} + A_{2g} + 2E_g + 3T_{2g} + 3T_{2g}$$

In X-Ray spectra of MX$_{6}^{2-}$ ions (M = Ru, Rh, Pd; X = F, Cl, Br, I) the low resolution of the halogen K-lines (Fig. 8) did not allow to determine a sequence of closely related ligand levels.

### Table 2 – Orbital energies and contributions of atoms to valence MOs of octahedral anions

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<td>- $\epsilon$, eV</td>
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<td>97</td>
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3.4 Electronic Structure of Chlorides and Bromides Anions

The 3a1g orbital is unoccupied in the compounds [TeXa]2−, [SbXa]2−, but two additional electrons in 3a1g of [SbCl6]3− cause an increase in the bond length of Sb-Cl from 2.44 Å in [SbCl6]− to 2.80 Å as a result of a decrease in the multiplicity of the Sb-Cl bond from 0.255 to 0.115.

A similar regularity is observed for antimony bromides: the multiplicity of the bond decreases from 0.738 to 0.482, the interatomic distances of Sb-Br increase from 2.63 to 2.97 Å. In tellurium compounds, two electrons in 3a1g of [TeCl6]2− cause an increase in the Te-Cl bond length from 2.37 Å in [TeCl6]2− to 2.61 Å due to a decrease in the Te-Cl multiplicity of the bond from 0.308 to 0.109. For tellurium bromides the multiplicity of the bond decreases from 0.297 to 0.126, the Te-Br interatomic distances increase from 2.58 to 2.79 Å.

Three lowest MOs 1αu, 1t_{2u}, 1e_{g} of anions [SbXa]− and [SbXa]3− contain the predominant contributions of halogen ns-AOs, but 1αu makes a notable contribution to Sb-X bonding due to Sb5s-Xns overlap, where n = 3 and 4 respectively for Cl and Br (Table 2, Fig. 3). Bonding MO 2a1g in [SbXa]3− has close contributions of metal 5s AO and Xnp. But in [SbXa]3− this orbital includes up to 80 % of antimony 5s AO and combination of halogen 3s (4s) and 3p (4p) orbitals. The contributions of np-orbitals enhance the Sb-X bonding, and the contributions of the ns orbitals (unlike 1αg) are antibonding.

The dominance of s-AO in the s-p-hybrid orbital of halogen led to the presence of a nodal surface between Sb and X in the MO 2a1g (Fig. 3). The main role in the covalent binding of Sb-X is played by 6 electrons of 2t_{1u} MO, which realizes the Sb5p-Xnp interaction. And 28 electrons of nonbonding MOs 1t_{2u}, 2e_{g}, 3t_{1u}, 1t_{2u}, 1e_{g}, localized on halogen atoms from 97 to 100 %, are important when considering the degree of ionicity of the bonds and the charge transfer process X → Sb in excited states.

According to the calculation the occupied in the anion [SbXa]2− HOMO 2a_{1g} is an antibonding combination of Xnp-orbitals and metal 5s-AO (16 % - [SbCl6]3−, 11 % - [SbBr6]3−). When occupying 3a_{1g}, the structure of 2a_{1g} changes markedly: the contribution of tellurium 5s AO increases to 61 % and 58 %, respectively, for compounds with chlorine and bromine, which is represented in the correlation diagram (Fig. 9).

The triply degenerate t-MOs of anions, due to lowering the symmetry, split into:

\[ t_{1u} \rightarrow a_{2u} + e_{u}, t_{2g} \rightarrow e_{g} + a_{1g}, t_{2u} \rightarrow a_{1u} + e_{u}, t_{1g} \rightarrow a_{2g} + e_{g} \]

or into:

\[ t_{1g} \rightarrow b_{2g} + a_{g}, t_{2u} \rightarrow b_{u} + a_{u}, t_{1u} \rightarrow a_{g} + a_{u} + b_{u}, a_{u} + b_{u}, b_{u} + a_{g} + b_{u} \]

At the same time, a relative sequence of electronic levels does not change, analogous to octahedral anions MX₆²⁻.

3.5 XPS Spectra Valence Bands Perovskite Cs₂TeCl₆

The intense narrow band 1 with maximum at 3.74 eV (Figure 10) in the spectrum of TeCl₆Cs₂ is due to a group of non-bonding Xnp levels of halogens correlating with the MOs 1t_{2u}²2e_{g}³3t_{1u}³1t_{2u}³2t_{1u}² of octahedron TeX₆²⁻. The bend 1' in the first band at 1.48 eV corresponds to TeX₆²⁻ 3a_{1g}² HOMO.

Band 2 corresponds to the bonding 2t_{1u}⁶ MO (Te5p + halogen Xnp). The bands 3 and 4 are due to the Cs5p MO, and their splitting into two bands is explained by the spin-orbital interaction, which is not taken into account by the DFT method. Band 5 with a maximum at 14.6 eV in X-Ray photoelectron spectrum (Fig. 10) corresponds to the anion MOs 2a_{1g}², 1t_{1u}⁶, 1e_{g}⁴.

The changes in the intensity and position of the va-
Valence-electron bands during the substitution of Cl by Br are due to the fact that binding energy of bromine 4s and 4p electrons decreases comparing to chlorine 3s and 3p electrons, and the ionization cross-section of Br 4p AO increases comparing to Cl 3p AO.

Fig. 10 – Valence bands of X-Ray photoelectron spectrum (a), theoretical spectrum (b) and partial densities (c) for Cs2TeCl6.

4. CONCLUSION

According to the experimental data and the calculation the 3a1g is the HOMO in molecular crystals studied, which is an antibonding combination of Xnp orbitals with a contribution of the halogen atoms of 85%. Previously this MO was believed to be a metallic nature primarily. It has been determined that in the anions the main role in the covalent metal-halogen binding is played by 6 electrons of 2t1u, 6 MO, and 28 electrons of non-bonding 1f2u+2e2u+3t1u+1t2g+1t1g MOs, localized mainly on halogen atoms. It is essential when considering the degree of ionicity of the bonds and the charge transfer processes in excited states. The transition from the 3a1g HOMO to the 4f1u LUMO, which corresponds to the states 1T1u and 2T1u, is responsible for the luminescence of the [MX6]2– anions.

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