

ESTIMATION OF THE PHOTOLYTICAL CENTRES IN AgBr

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The 5.13 eV peak of the dominant absorption band of AgHal can be considered as due to the bond energy E_b of d-states of Ag^+ . The 4.25 eV peak characteristic of AgBr can be determined as $E(\text{electron affinity } E_a(\text{Br}^0), E_b(\text{Ag}^+))$, where $E(a,b)$ is the mean of the quantities a and b. If $E_a = 3.37$ eV, it follows that $E = 4.25$ eV, that corresponds to the Low-Energy d-p States (LES). High-Energy States (HES) 5.57 and 6.01 eV and LES are in balance about $E_b(\text{Ag}^+)$. While Ag_n^+ is at the centre of the NaCl-like lattice, the dynamic equilibrium state can be considered as interference of the centres $Ag^+ - Ag_n^+$ and Ag^+ . HES of that centre is calculated as $E(E_b(\text{Ag}^+), E_a(\text{Ag}_n^+))$. If $E_a(\text{Ag}^+) = 3.9$ eV [1], we get 4.515 eV. Similarly, energy of d-p-d states is calculated as 4.075 eV. Mixing with HES (5.57 eV) yields 4.822 eV which is characteristic of AgBr from the melt. Light irradiation and Coulomb interaction of Ag^+ and Ag_n^+ may result in a shift of Ag^+ so that $Ag^+ - Ag^+$ is symmetric about the lattice site. This lowers LES by Coulomb energy $E_c = 0.06$ eV [1,2] at the $Ag^+ - Ag^+$ distance 2.89 - 2.9 Å [1,2]. Mixing d- and d-p-d states in this centre leads to the magnitude of 4.571 eV which corresponds to HES. Mixing with LES (4.015 eV) yields 4.29 eV characteristic of AgBr. When Ag_n^+ is in the centre of face-centred cubic (fcc) AgBr lattice, the linear centre $Ag^+ - Ag_n^+ - Ag^+$ is formed with ion-ion distance 2.89 Å. LES is lowered by $2E_c$ and therefore we get 3.955 eV. Dynamically equilibrium d-s state is calculated as $E_a(\text{Ag}_n^+) - 2E_c$ or $E(E_b(\text{Ag}^+), E_b(\text{Ag}_3^+))$ where $E_b(\text{Ag}^+) = 2.43$ eV. In both cases we obtain 3.78 eV which corresponds to "plasmon" states in AgHal. Electron density shift from Br^- to $2Ag^+$ or $3Ag^+$ is responsible ($2Ag^+ - Br^0$ and $Br^0 - (3Ag^+) - Br^0$ centres denoted by A^+ and B^+). As the density rearranges, neutral centres A^0 and B^0 are possible as well. Energies of d-p-s states for A^+ and B^+ are calculated as $E_b(A^+) = E(E_b(\text{Ag}_2^+), E_a(\text{Br}^0))$ and $E_b(B^+) = E(E_b(\text{Ag}_3^+), E_a(\text{Br}^0))$. Taking $E_b(\text{Ag}_2^+) = 2.26$ eV, $E_b(\text{Ag}_3^+) = 3.66$ eV and $E_a(\text{Br}^0) = 3.37$ eV we get 2.815 and 3.515 eV for A^+ and B^+ respectively. The magnitudes 4.572, 4.015, 2.815 and 3.515 eV calculated above coincide with the known fluorescence excitation maxima. In the same way we obtain $E_b(\text{Ag}_2) = 1.62$ eV and $E_b(\text{Ag}_3) = 2.43$ eV. From the symmetry of the lattice it follows that $E_b(B^+)$ can be estimated as $E_b(\text{Ag}_3^+) - 2E_c = 3.54$ eV. This magnitude is also obtained as $E(E_b(\text{Ag}^+), E_a(\text{Ag}_2^+))$, i.e. corresponds to the dissociated centre Ag_3^+ , being characteristic of d-s state of B^+ centres in fcc lattice.

In the case of non-linear displacement of Ag^+ , the magnitude $E_b(\text{Ag}_3^+) = 2.495$ eV is used, which coincides with the absorption maximum of bipyramid Ag_6^+ centres in the compounds like γ -AgI. Here, $E_b(B^+) = E(E_b(\text{Ag}_3^+), E_a(\text{Br}^0))$ that yields 3.406 eV.

In the same way, from the values $E_b(\text{Ag}_2) = 1.62$ eV and $E_b(\text{Ag}_3) = 2.43$ eV, and also $E_a(\text{Br}^0)$, we obtain $E_b(A^0) = 2.495$ eV and $E_b(B^0) = 2.90$ eV. At the non-linear displacement of Ag^+ , from $E_b(\text{Ag}_3^0) = 2.28$ eV it follows $E_b(B^0) = 2.825$ eV.

For A^+ and B^+ centres being in equilibrium with the lattice, the magnitudes $E_a(\text{Ag}_2^+) = 1.95$ eV and $E_a(\text{Ag}_3^+) = 1.75$ eV are used [1,2] that yields the d-p-s levels 2.66 and 2.55 eV which coincide with the absorption edges for AgBr at 77 K and 295 K. If the $Ag^+ - Ag^+$ distance is maximised up to 4.07 Å, Ag^+ centre can be considered as the structural unit of the fcc lattice. In doing so $E_b = E(E_a(\text{Ag}_2^+), E_a(\text{Ag}_n^+))$ or $E(E_a(\text{Ag}_2^+) \text{ and } E_a(\text{Br}^0))$ from the other hand. That yields 3.148 eV. For NaCl lattice, B^+ centre without Ag_n^+ can be considered as a structural unit. The energy of d-p interactions in AgBr is calculated as the difference between LES (4.25 eV) and $E_a(\text{Ag}_n^+) = 3.9$ eV that yields $E_b(B^+ - Ag^+) = 3.165$ eV. The magnitudes 3.148 and 3.165 eV correspond E_g for ideal AgBr. Actually, the dynamically equilibrium state is as superposition of B^+ and B^0

centres that correspond the known value of $E_g = 2.706$ eV. At thermo- or photoionisation of the centres the level of d-p-s states can be estimated as $E(E_b(A^+) \text{ or } E_b(B^0), E_{bg})$ at 77 K that yields two magnitudes: 2.7375 and 2.7425 eV where the difference 2.5 meV is the characteristic of the electron density fluctuations. Note that 2.74 eV coincide with the maximum of the photoconductivity spectrum. Close magnitudes of the Ag^+ and Br^0 radiuses (1.13 and 1.14 Å) and $E_a(Ag^+)$ and $E_a(Br^0)$, as well as, $E_b(A^+)$ and $E_b(B^0)$ suggest Coulomb equivalence for Ag^+ and Br^0 . That allows us to estimate the energy level for Br^0 in the field of $2Ag^+$ as $E_a(Br^0) - 2E_c = 3.25$ eV. In this case the magnitudes $E_b(A^+) - 2.74$ eV = 0.075 eV and $E_b(B^0) - 2.74$ eV = 0.085 eV corresponds the magnitudes E_c Coulomb interactions between ($2Ag^+$) or ($3Ag^+$) and Br^0 and can be considered, as well as 0.06 eV, as some kind of the principal values of E_c . Really, at Coulomb interactions between Ag_3^+ and Br^0 as a hole, the level of d-p-s states lowers from 3.432 to 3.367 eV that nearly coincides with $E_a(Br^0)$. Photoionisation of the dynamically equilibrium centres at the levels 2.7375 and 2.7425 eV lowers the energy level by the above magnitudes of E_c that coincides with the exciton maxima of the luminescence bands in AgBr. It is believed that primary photolytical centre Ag^{++} is responsible for the short-lived absorption bands of AgBr 0.9 and 1.3 eV. The luminescence spectrum of AgBr reveals the following maxima: 2.83, 2.68, 2.45 and 2.20 eV. One can believe that 0.9 eV band is a result of the shift of E_{bg} in the field of Ag^{++} by 1.76 eV. From the energy balance ($3.37 + 1.76 = 5.13$ eV), there follows the shift of electron density from $E_a(Br^0)$ to the level $E_b(Ag^+)$. In this case, the 2.83 eV band corresponds to the transition between the levels 5.57 and 2.74 eV. Other luminescence bands correspond to the transitions $E_{bg} - E_b(Ag_n^+)$ and $E_a(Ag^{++}) - E_a(Br^0)$. Photogeneration of Ag^{++} in the field of Ag_n^+ may lead to the pair A^+ and B^+ centres formation. The generation of Ag^{++} by quanta of 3-4 eV, as well as the generation of such centres in the field of Ag_n^+ (the 2.66 and 2.47 eV luminescence bands) suggest the localisation of the excitation as a sum of energy of two or more quanta in the defect field. Possible mechanism of the localisation appears to be as the interaction of LES and HES in one centre with the resulting addition of the vibration energy.

On low energy excitation of AgBr the following transitions are possible: $E_a(Ag_2^+) - E_a(Ag_n^+)$: 1.95 eV; $E_a(Ag_n^0) - E_a(Br^0)$: 1.95 eV; $E_a(Ag_n^0) - E_b(B^+ - A^+)$: 1.55 eV where $E_b(B^+ - A^+)$ is the bond energy of dynamically equilibrium state between the centres ($2Ag^+$) and ($3Ag^+$) in non-linear case. The above luminescence bands are observed in AgBr crystals at the excitation of 2.81 eV, in which, in accordance with the intensities of the bands, the energy balance is reached as 3 absorbed to 4 emitted quanta (1.55 eV) and one quantum of 1.95 eV. It can be noted that the balanced transition to the excited state corresponds to the 6-electrons transition from E_{bg} (2.66 eV) to the level $E_a(Ag_n^0) = 1.30$ eV. The difference between the absorption (8.43 eV) and emission (8.15 eV) appears to be 0.28 eV that coincides with E_c in the system of A^+ and B^+ centres. Really, this suggests the possibility of the existence of "bipyramidal microphases" with partially distorted fcc structure in NaCl lattice of AgBr.

In the discussed system of Ag centres there exist two regions of overlapping of the electron states: 4.60 - 3.40 and 3.10 - 2.65 eV responsible for d-p-d and d-p-s interactions which thereby explains the possibility of the generation of Ag^{++} by the quanta > 3.40 eV only, and also a profound minimum in the region of 3.30-3.20 eV in the absorption spectrum.

We can state now that in the Ag compounds studied the electron transitions at the absorption edge are due to the intrinsic centres including biographic defects even for rated pure systems.

- [1] V.A. Voll, *Tekh. Fiz. (Russia)*, **64** (1994), 115-119 (Russ)
- [2] V.A. Voll, *Fiz. Tekh. Polupr. (Russia)*, **29** (1995), 2071-2077 (Russ)