

Sulfur Sensitization of AgBr Emulsion: Nature of Sensitivity Centers

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Abstract

The nature of the sensitivity centers that appear at sulfur sensitization of cubic and octahedral AgBr emulsions has been investigated by the luminescence method. Photoluminescence (PL) spectra ($T \geq 4.2\text{K}$) and photoluminescence excitation spectra of monocrystal AgBr(Ag₂S) with different concentrations of Ag₂S have been studied for comparison. The emission spectra of AgBr(Ag₂S) ($T < 25\text{K}$) have the 563nm band with multi-phonon structure. The band 563nm is S²⁻-bound exciton emission. This band does not appear at sulfur sensitized AgBr emulsion microcrystals (MC), suggesting that (S²⁻Ag_i⁺) complexes and their dimers do not form at sulfur sensitization. Based on luminescence studies, it is found that in the case of the cubic AgBr MC sensitivity centers are either (Ag₂S)_pAg⁺ or (Ag₂S)_q ($q > p$) clusters with the size $d > 20\text{\AA}$, whereas in the case of the octahedral emulsions the sensitivity center is the (Ag₂S)₂ dimer located near the positively charged MC surface defect. It also is determined that this dimer is the 0.46eV electron trap.

Introduction

The literature on sulfur sensitization of silver halide photographic emulsions contains a number of models for the sensitivity centers that emerge during sensitization. Such impurity centers determine appearance of specific low temperature luminescence bands, and, thus, the nature of sensitivity centers can be studied using the luminescent method (see e.g. Refs. 1, 2).

Experimental

1. It has been proposed [3, 4] that at sulfur sensitization S²⁻ ions can occupy the surface anion sites of the AgBr lattice, and their additional negative charge is compensated by nearby interstitial silver ions (Ag_i⁺). In this case it is possible not only the formation of single complexes, [S²⁻Ag_i⁺], but also their dimers [4], or even larger structures, [S²⁻Ag_i⁺]_n [3]. According to the approach proposed in Refs. [3, 4], the [S²⁻Ag_i⁺]_n centers, or their dimers [4], are able to assemble in their immediate vicinity photolytic silver, and, therefore, they can play a role of sensitivity centers.

Complexes of the [S²⁻Ag_i⁺]-type are formed also in AgBr monocrystals doped with Ag₂S [5]. Therefore, we used the AgBr monocrystals doped with different concentrations of Ag₂S as a model system in our photoluminescent (PL) studies, results of which have been compared with the PL data from sulfur sensitized AgBr microcrystals (MC).

At $T = 4.2\text{K}$ the PL of AgBr(Ag₂S) monocrystals exhibits two bands with $\lambda_{\text{max}} = 563\text{-}565\text{nm}$ and $\lambda_{\text{max}} = 640\text{nm}$ [6-8]. It has been noted in Ref. 7 that the short-wavelength edge of the 565nm band

exhibits plateaus (Fig. 1) whose spectral positions are at 5339Å (2.322eV), 5378Å (2.305eV), 5422Å (2.287eV), 5463Å (2.270eV), and 5502Å (2.253eV). The energy difference between the plateaus is 0.017eV, which is the same as the energy of the AgBr LO-phonon.

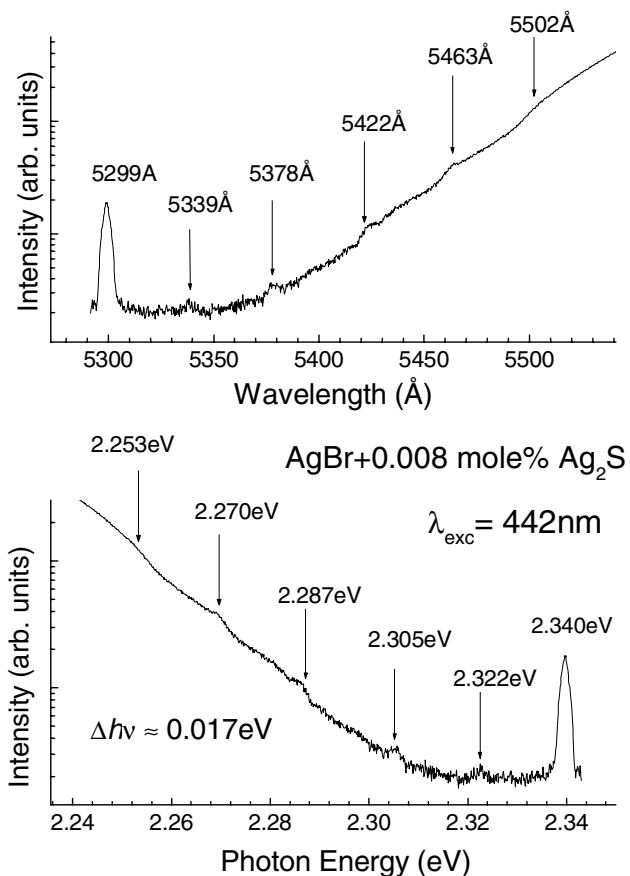


Figure 1. Multi-phonon structure of the 563-565nm PL band.

To explain these results, we note that the 4.2K PL of nominally pure AgBr monocrystals exhibits the band with $\lambda_{\text{max}} = 497\text{nm}$ characterized by the multi-phonon structure, which is determined by the electron-LO-phonon interaction. This PL band is due to an Γ -bound exciton (AgBr always contains some residual Γ ions). Thus, since both S²⁻ and Γ are isoelectronic impurities in AgBr, the existence of the plateau structure in the 565nm band allows one to assume that this band is due to S²⁻-bound exciton and, as in the case of Γ ions, electron-phonon interaction must be taken into account during the analysis. Here, the zero-phonon

(ZP) line is observed at $\lambda = 529.9\text{nm}$ (2.340eV) (Fig. 1). Such a conclusion is further supported by PL excitation (PLE) studies.

The PLE spectrum of the 565nm band has three maximums at $\lambda = 468\text{nm}$, 497nm, and 530nm [7, 8] (Fig. 2). The 468nm maximum is very close to the AgBr fundamental absorption edge. Thus, this maximum is due to light absorption by Br^- ion, located next to the bulk S^{2-} ion, followed by the energy transfer from the

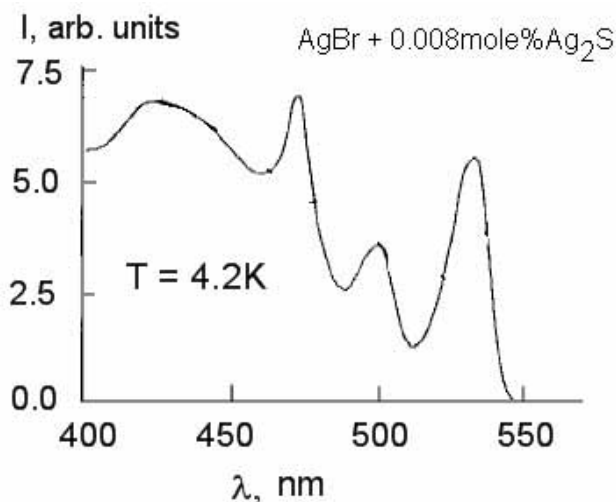
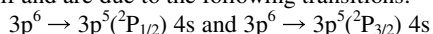


Figure 2 Photoluminescence Excitation Spectrum of the 563-565nm PL band

excited $(\text{Br}^-)^*$ ion to the S^{2-} ion. The maximums at 497nm (2.49eV) and 530nm (2.33eV) are owing to the absorption by S^{2-} ion itself and are due to the following transitions:



Based on these results we found that the constant of spin-orbit interaction for S^{2-} ions is 0.16eV.

Next we show (Fig. 3) the PL spectra for $\text{AgBr}(\text{Ag}_2\text{S})$ monocystals excited by $\lambda = 495\text{nm}$ or $\lambda = 530\text{nm}$ light. As expected, two bands with $\lambda_{\text{max}} = 563\text{nm}$ (2.20eV) and 605nm - 606nm (2.04eV) are observed, for the lowest excitonic state has configuration $3p^5 4s$, whereas $3p^5$ state has the total angular momentums $j=3/2$ or $j=1/2$.

The increase of the sample temperature results in the quenching of the 563nm and 606nm bands and in the appearance (at $T > 25\text{K}$) of three new PL bands with $\lambda_{\text{max}} = 570$, 615 and 690nm (Fig. 4; in this case the 530nm monochromatic light was used for excitation). The PL bands with $\lambda_{\text{max}} = 570\text{nm}$ (2.175eV) and 615nm (2.016eV) are observed only below 40K (Fig.4).

We suggest that these two bands are due to the exciton localized at S^{2-} ion located in the sub-surface layer of AgBr (surface exciton). Indeed, the energy difference between these two bands is 0.16eV, which corresponds to the spin-orbit splitting of the $3p^5$ level in the excited S^{2-} ion. Thermal decomposition of S^{2-} -localized excitons (bulk and surface) is accompanied by the appearance of the PL band with $\lambda_{\text{max}} = 690\text{nm}$ (1.80eV) (Fig.4).

It is important that computer models [9] have predicted that the energy of the singlet-singlet transition in a $(\text{Ag}_2\text{S})_2$ dimer, located on (001) face of AgBr, is 2.33eV, whereas that of the singlet-triplet transition is 1.86eV. Thus, it is possible to assume that the 690nm (1.80eV) band corresponds to the triplet-singlet

transition in the excited $(\text{Ag}_2\text{S})_2$ dimer that is located in the vicinity of structural defects on the (001) face of AgBr lattice. The upward bending of the energy bands near the surface of AgBr monocystals facilitates the appearance of the the triplet level of

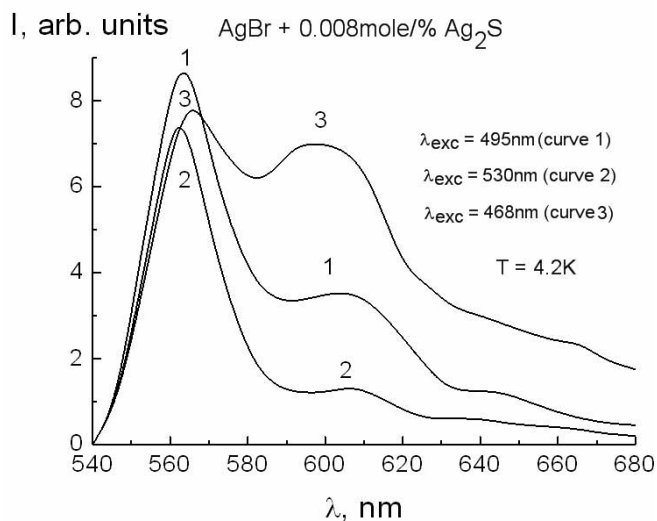


Figure 3. Photoluminescence Spectra

$(\text{Ag}_2\text{S})_2$ below the bottom of the AgBr conduction band.

If the 468nm monochromatic light is used as excitation, the PL band with $\lambda_{\text{max}} = 565\text{nm}$ as well as very broad band in the orange region of the spectra will appear (Fig. 3, curve 3). This data suggests that the excited Br^- -ion may transfer energy not only to the nearby S^{2-} -ion but also emit light by itself (the band with $\lambda_{\text{max}} = 585\text{-}590\text{nm}$). The latter can be observed at 4.2K even in the nominally pure AgBr monocystals. If the local excess negative charge is required (in the case of $\text{AgBr}(\text{S})$) it is provided

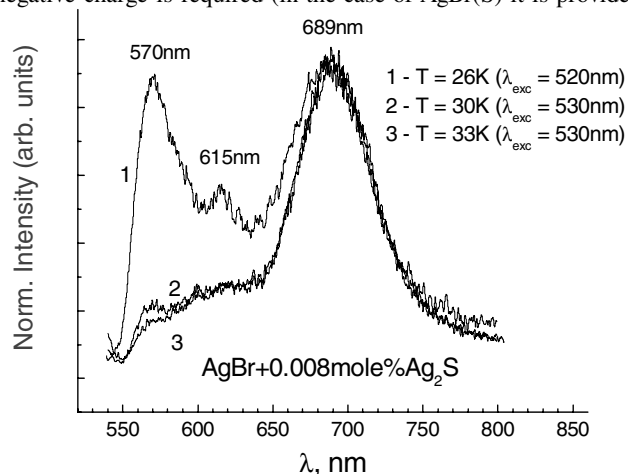


Figure 4 Photoluminescence Spectra

by S^{2-} ions) for such an emission, then in pure AgBr crystals this PL can originate from Br^* ions, which locate next to a cation vacancy.

The increase in the sulfur ion concentration in AgBr leads to the changes in the PL of AgBr monocystals (Fig. 5). In this case the band with $\lambda_{\text{max}} = 585\text{-}590\text{nm}$ ($T = 77\text{K}$) appears, and it shifts

to the shorter wavelengths with decreasing temperature (Fig. 5). Apparently, this emission is due to the creation of centers that have two S^{2-} -ions next to each other and where the excess negative charge is compensated by two nearby interstitial silver ions [7b]. At $T = 4.2K$ the dominant emission ($\lambda_{max} = 565nm$) is due to the individual S^{2-} ions that are part of the $S^{2-}-Ag_i^+$ complexes. An increase in the temperature results in the

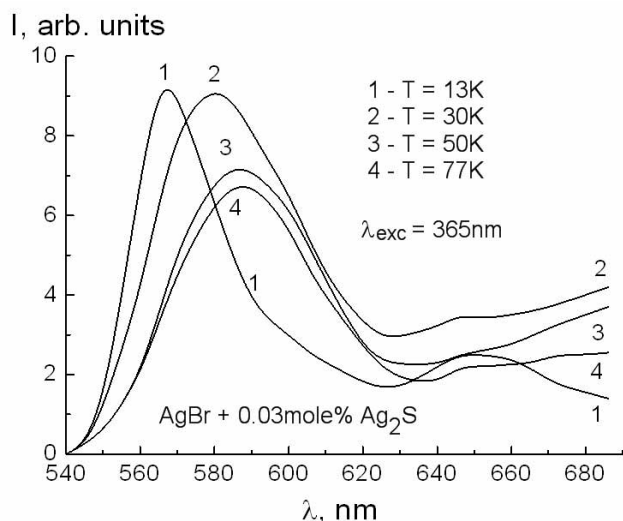


Figure 5. Photoluminescence Spectra

quenching of this PL, and at 77K only the PL due to $(S^{2-}-Ag_i^+)_2$ dimers (the 585-590nm band) is observed. The dimer PL follows the Shen-Klassen mechanism, where a conduction band electron recombines with the hole localized at the dimer [7b].

It is important to note that none of the details either of the PL ($\lambda < 650nm$) or of the PLE from $AgBr(Ag_2S)$ monocrystals is observed in the PL from sulfur-sensitized silver-bromide emulsions. Thus, sulfur-silver complexes do not form during sulfur sensitization, and, therefore, they are not responsible either for photoluminescence from the sensitized MC or for the formation of sensitivity centers of the sulfur-sensitized silver-bromide emulsions.

2. At $T = 4.2K$ the PL spectrum of the emulsion $AgBr$ MC consists, in general, of two bands with $\lambda_{max} = 497nm$ and $590nm$ (Fig. 6, curve 1). The 497nm is due to I -localized exciton. The 590nm band emerges only if the synthesis of $AgBr$ MC has been done in gelatin. If these MCs are synthesized in polyvinyl alcohol or EtOH, the orange-red emission does not appear (Fig. 6, curve 2; see also Ref. 7a). It is important to note that this emission can be excited not only by the light from $AgBr$ absorption ($\lambda < 460nm$) but also by the light with $\lambda > 460nm$.

To explain this result one must remember that gelatin always includes sulfur-containing impurities, which when reacting with Ag^+ -ions (these ions are introduced during MC synthesis) form both Ag_2S molecules and $(Ag_2S)_2$ dimers. The computer simulations [9] have predicted that the energies of singlet-singlet ($S_0 - S$) and singlet-triplet ($S_0 - T$) transitions in Ag_2S molecule are 2.57eV and 2.10eV, respectively. For the dimers, these are 2.33eV and 2.00eV, respectively [9]. This allows to assume that if the light with $\lambda = 530nm$ (2.33eV) is used for an excitation, the

$(Ag_2S)_2$ would phosphoresce in the orange-red spectral region. If the excitation is by the light from the $AgBr$ absorption, the emission from I -bound excitons ($\lambda = 497nm$, $h\nu = 2.5eV$) is reabsorbed by Ag_2S molecules in gelatin resulting in both fluorescence and phosphorescence (the orange-red band). Therefore, the orange-red luminescence of emulsion layers is partially due to gelatin Ag_2S molecules and dimers. This conclusion is in good agreement with an experimentally observed life time (up to 1s) of this emission.

In order to further verify this conclusion we studied the PL of gelatin solutions mixed with low concentration solution of $AgNO_3$ and Na_2S (sample A), since Ag_2S molecules and corresponding dimers can be formed in gelatin solution due to reaction of Ag^+ -ions with S^{2-} . The excitation of such solution (frozen, $T = 4.2K$) with the 520nm light exhibited, as expected [9], two PL bands with $\lambda_{max} = 540nm$ and $590nm$ (Fig. 6), which have origin in transitions $S \rightarrow S_0$ and $T \rightarrow S_0$ in $(Ag_2S)_2$ dimers, respectively.

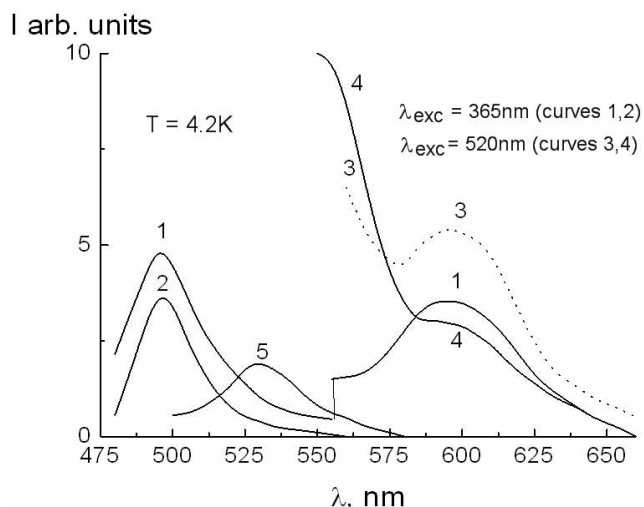


Figure 6. Photoluminescence Spectra of $AgBr$ emulsion (curves 1, 3), $AgBr$ MCs in 96% EtOH (curve 2) and sample A (curve 4). Curve 5 is PLE Spectrum of the 600nm band of sample A.

If the cubic $AgBr$ MCs synthesized in gelatin solution are cleaned of gelatin by centrifugation, then in the PL ($T = 4.2K$) one can observe two bands with $\lambda_{max} = 497$ and $600nm$ s (Fig. 7, curves 1 – 3). As well known, the interaction of gelatin sulfur-containing impurities with $AgBr$ leads to formation of surface Ag_2S molecules, which can migrate over the surface and congregate into dimers, trimers, and clusters (molecules and dimers of Ag_2S from gelatin can also adsorb on MC surface).

In order to determine the nature of the center that is responsible for the band with $\lambda_{max} = 600nm$ we note the following:

a) The change of the excitation intensity by a factor 100 does not lead to a spectral shift of this PL band (Fig. 7, curves 1 – 3); this corresponds to the case when emission is due to the recombination between a conduction band electron and a localized hole (transition 1) or due to the recombination between a valence band hole and a localized electron (transition 2).

b) Irradiation of the sample by infrared (IR) light results in quenching of the orange-red emission without PL flash. In the case of AgBr this is characteristic of transition 2 (see, for example, Ref. 2; the IR light releases the electron from the recombination level).

Since Ag₂S molecules adsorbed on the AgBr surface do not create localization levels for electrons [9], it is possible to assume that the band with $\lambda_{\text{max}} = 600\text{nm}$ is due to the recombination

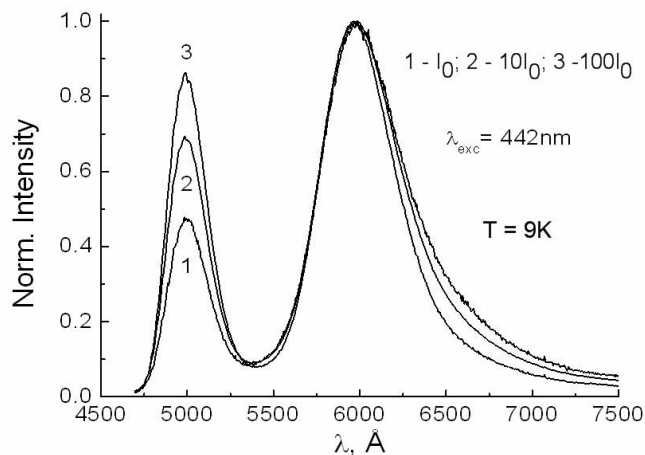


Figure 7. Photoluminescence Spectra of cube MC AgBr emulsion at different excitation intensity (I_0)

between a hole from the AgBr valence band and the electron localized at a $\text{DK}(\text{Ag}_2\text{S})_2$ center [9] (here $\text{DK}(\text{Ag}_2\text{S})_2$ center is a $(\text{Ag}_2\text{S})_2$ dimer, which is located next to a positively charged surface defect in AgBr [9]). The 600nm band has a very large full width at half maximum (FWHM), which suggests a relatively strong electron-phonon interaction. In this case the energy of zero-phonon transition (E_0) can be estimated from the short wavelength edge of the band. For the 600nm band, this corresponds to $\lambda \approx 550 - 555\text{nm}$ (i.e., $E_0 \approx 2.24\text{eV}$). The same value for E_0 is obtained with the use of the Hung-Rhys theory [10]. Furthermore, since the valence band hole recombines with a neutral center (i.e., $[\text{DK}(\text{Ag}_2\text{S})_2]$), the recombination takes place without the hole's initially occupying an excited level. Thus, using values of the AgBr bandgap ($E_g = 2.7\text{eV}$, $T = 4.2\text{K}$) and $E_0 = 2.24\text{eV}$ we estimate that $\text{DK}(\text{Ag}_2\text{S})_2$ creates a localization level for an electron with the depth $E_D = 0.46\text{eV}$. This value is in good agreement with that given in Ref. 9, based on computer calculations. Thus, as an electron trap with $E_D > 0.4\text{eV}$, a $\text{DK}(\text{Ag}_2\text{S})_2$ center can play a role of sensitivity center [9].

The described process will, obviously, occur during sulfur sensitization of those AgBr MCs whose surface has defects that restrict migration of Ag₂S molecules, and therefore prevent their aggregation into relatively large ($d > 20\text{Å}$) clusters. Such MCs are octahedral and tabular MCs as well as the MCs obtained by the single-jet precipitation. This is in good agreement with previously reported [1] simultaneous increases (after sulfur sensitization of AgBr(I) emulsion) in the intensity of the orange-red photoluminescence and the sensitivity.

3. The Ag₂S molecules created during sulfur sensitization of cubic AgBr MCs can easily migrate on the surface and form large

$(\text{Ag}_2\text{S})_n$ clusters. Such clusters of various sizes are responsible for an appearance of the near IR luminescence bands [2]. Using the approach proposed by Brus [11] one can find the energy levels of electrons and holes in the $(\text{Ag}_2\text{S})_n$ clusters in the reference to the AgBr energy bands. The calculations given in Ref. 12, as well as our own estimations, have shown that for the $(\text{Ag}_2\text{S})_n$ clusters with $d < 20\text{Å}$ 1S_e level (the lowest energy electronic state in a cluster) is in the AgBr conduction band, whereas 1S_h level (the lowest energy hole state in a cluster) is above the AgBr valence band. Thus, such clusters cannot localize electrons, but are good traps for holes. The traps for electrons with $E \sim 0.4\text{eV}$ are created only by the clusters with $d > 25\text{Å}$ (the 1S_e levels of such clusters is below the AgBr conduction band by more than 0.4eV). These clusters play the role of the sensitivity centers in the case of cubic AgBr MC [2]. Moreover, such large clusters can adsorb Ag^+ , which dramatically increase electron capture cross section [2].

Since in the $(\text{Ag}_2\text{S})_n$ clusters with $d < 20\text{Å}$ the 1S_e level is in the AgBr conduction band, the photogenerated electrons will end up at the bottom of the AgBr conduction band; in this case the photoluminescence appear as a recombination between this electron and the hole localized at the $(\text{Ag}_2\text{S})_n$ cluster. The light absorption by the $(\text{Ag}_2\text{S})_n$ clusters with $d < 20\text{Å}$ also controls the impurity sensitivity (between 460nm and 700nm [13]) of sulfur sensitized emulsions. If the 1S_e level of a $(\text{Ag}_2\text{S})_n$ cluster (nanocrystal) is located under the conduction band of AgBr (the size of a cluster, $d > 20\text{Å}$), then the luminescence of an excited cluster is formed due to the $1\text{S}_e-1\text{S}_h$ transition. The energy of the $1\text{S}_e-1\text{S}_h$ transition decreases with the increase in the cluster size [2, 11].

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