Radioluminescent Properties of CdS(Ag) Crystals

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Abstract

The radioluminescent proporties of silver-doped cadmium sulphide, CdS(Ag), crystals excited by 5.5 MeV α-particles from an ^{241}Am radioactive source have been investigated. The emission spectra, decay profiles and thermal quenching curves were obtained accurately at temperatures between 80 K and 300 K. Two main radioluminescent emission bands centered at about 5760 Å and 5940 Å were observed. Their decay curves were found to be fast and nonexponential. From the thermal quenching of radioluminescence, the activation energies of centers responsible for these emissions were determined. The results are interpreted as the radioluminescence is possibly due to donor-acceptor pair recombinations.

PACS codes / Keywords: 7860.-b / Radioluminescence, CdS(Ag), Recombination

1. Introduction

Cadmium sulphide crystals (pure and doped) are of interest for their luminescent, photoconductive and acoustoelectric properties. For most purposes a substantially doped sample is required. The luminescent proporties of pure and doped CdS have been studied extensively [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15]. The luminescence spectrum of Ag-doped crystal usually gives a broad structureless band centred at about 6100 Å [4, 9, 10]. Schon [1] and Klasens [2] suggested recombination between free electrons and holes trapped at impurity centres for this emission, while Lambe and Klick [3] based their model on the simultaneous measurements of photoconductivity and photoluminescence. Van Gool [4] investigated Ag-activated CdS with Ga or Cl as coactivator and found two bands with maxima at 6200 Å and 7300 Å for the low temperature fluorescence. He reported that high Ag and low coactivator concentration favors the high energy band,

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otherwise the low-energy band predominates. This led van Gool to suggest that the centre responsible for the short-wavelength band is an associate of at least two lattice defects. Using time-resolved spectroscopy, Brown et al [6] reported three different emissions in the 6100 Å region, and were able to distinguish between them because of different decay times. They proposed a donor-acceptor pair model for the Ag emission, without specifying distant or associated pairs, with interstitial Ag as a donor. Emission in the 6100 Å region was also observed in some pure CdS crystals [6, 7, 8]. This observation caused Lehman [7] to doubt the interpretation that the 6100 Å emission originates from Ag centres. Later, Colbow et al [9] removed this uncertainty by proving that the Ag centre responsible for the 6100 Å emission is associated with another impurity, but less likely with a native defect. Further, they also observed a new emission (5600 Å) which arises from bound-to-bound recombination at distant donor-acceptor pairs with Ag as an acceptor. Rizakhanov et al [10] obtained the orange band maxima in the range $h\nu = 2.0$ - 2.15 eV (6200 Å - 5760 Å) at 77 K using different impurity concentrations in CdS crystals. They determined energy positions responsible for the orange luminescence by attributing them to donor-acceptor pairs, consisting of a donor with a level at $E_c - 0.23$ eV and an acceptor at $E_v + 0.26eV$. Emirov et al [11] proposed a model of complex trimer centre responsible for the orange luminescence from the polarization characteristics of the luminescence spectra in the range 1.8-2.2 eV.

In spite of the characteristic band of orange luminescence with maxima in the range $h\nu = 2.0 - 2.15$ eV and some other aspects of CdS(Ag) have been systematically investigated from 1955 on, however the physicochemical nature of the luminescence centres and the mechanism of the electron transition responsible for the radiative emission still preserve their complexity. In this work, we measured the emission spectra, decay profiles and thermal quenching curves of radioluminescence in our Ag-doped CdS crystals. These measurements give information about recombination mechanisms responsible for the luminescence centers in such crystals.

2. Experimental

Single crystals of CdS containing Ag were grown by sublimation in a flow of argon in the Applied Physics and Electronics Department of Durham University by the group of Dr. J. Woods. The charge was prepared from powder by a preliminary sublimation process. Silver was incorporated into the stream of argon flowing over the charge. The concentration of silver was rather high ($\sim 10^{18} - 10^{19} cm^{-3}$) [16]. Further details of crystal growth are given elsewhere [17]. A needle-type ^{241}Am radioactive source was used for excitation. The Am was deposited on one face of a holder, and found to have an activity of 1 μ Ci, emitting 5.5 MeV α-particles.

The single photon counting technique (SPCT) was used to measure the radioluminescent spectra, decay profiles and thermal quenching curves. It was specially developed for radioluminescence measurements and based on single photon counting detection [18]. The use of this popular technique as both an analytical and research tool has increased markedly in recent years [19].

The sample was placed in a vacuum cryostat, so that its temperature was measured easily between 80 K and 300 K by a fitted thermocouple. For spectral distributions, an adjustable monochromator was used (between the sample and stop-photomultiplier tube, type 56AVP and 9816QB). It is a graded interference filter (MS-1, 4000-7000 Å) which has a wide bandpass of about 300 Å. The wavelength control was carried out manually with a fitted screw. The filter unit also possess a complementary function of variable slit, which is specially required for noise measurements.

The spectral measurements were corrected for the photomultiplier response. For this, the noise pulses were measured simply by closing the adjustable slit, thereby completely blanking the stop-photomultiplier. Then, noise rates were subtracted from the recorded data, before they were plotted.

3. Results and Discussion

Figure 1 shows the spectral distribution of α-induced radioluminescent emission for the time range of $R = 0 - 1\mu s$ and $R = 0 - 4\mu s$ in CdS(Ag) crystals with cleaved surfaces at 90 K. The vertical axis illustrates the energy spectra which denotes the relative energy or number of photons emitted per unit wavelength versus wavelength. As seen from the $R = 0 - 1\mu s$ spectra, there are two main emission bands peaked at about 5760 Å (2.15 eV) and 5940 Å (2.08 eV). The 5760 Å emission band has a broader spectral distribution than that of 5940 Å emission band. Further, some interesting variations were also observed in the emission spectra when the time range (R) of time-to-pulse height converter (TPHC) was changed. If R is decreased (i.e., the system is now sensitive to only fast photons), the 5940 Å emission band starts to dominate and the 5760 Å emission band disappears. However, if R is increased, say $4\mu s$ as shown in Figure 1, the high wavelenth emission band (5940 Å) disappears and only one single broad emission band (5760 Å) dominates. This means that the radioluminescence center responsible for 5940 Å emission band has a shorter lifetime than that of 5760 Å emission band. The measurements of the decay profiles of the radioluminescence intensities just in the following will give support to the validity of this conclusion. For the $R = 0 - 4\mu s$ spectra, a fullwidth value of about 320 Å at half maximum was determined.

However we did not markedly observe the characteristic high energy bands (edge emissions) reported by others [8, 12, 13, 14, 15] at low temperatures. The reason may be our low temperature limit (80 K). Further, the 6100 Å emission present in conventionally Ag-doped CdS crystal was not also observed in our measurements. However this is not the case since the peak positions of the emission bands could be shifted due to the type of excitation and the Ag concentration [9, 11].

Figure 2 shows the decay of the radioluminescence intensity I(t) of CdS(Ag) after excitation, i.e., I(t) versus time (t), for different emissions at 110 K. From the decay profiles, the $t_{1/e}$ and t_{1/e^2} decay times (the times taken for the radioluminescent intensity to decrease to $1/e$ and $1/e^2$, respectively, of its initial value) were derived to be about 8.1 ns and 91.2 ns for 5580-5640 Å, 6.5 ns and 15.5 ns for 5760 Å, 3.2 ns and 6.5 ns for totol light, and, 3.1 ns and 5.5 ns for 5940 Å, respectively. These decay times were found to be

almost temperature independent [18]. Clearly, the decay processes in CdS(Ag) crystals are very fast and also non-exponential, the ratio of $t_{1/e}$ to t_{1/e^2} being about 0.09, 0.42, 0.49, and 0.56, respectively as before. The observed fast and non-exponential decay may be due to the higher ionizing character of 5.5 MeV α-particles used for excitation [20].
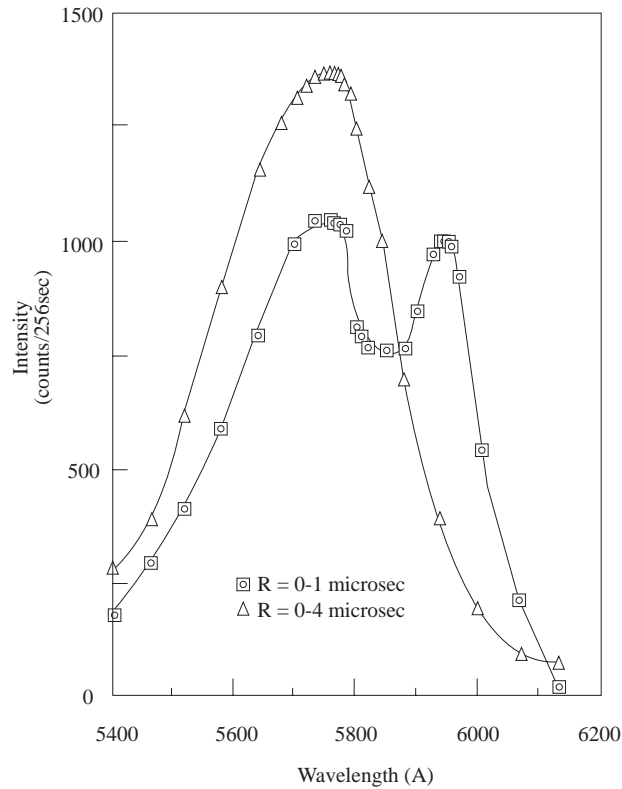

Figure 1. Radioluminescence spectrum of CdS(Ag) at 90K, for the time ranges of $R = 0 - 1\mu s$ and $R = 0 - 4\mu s$.

In Figure 2, the 5760 Å emission band has larger decay times than those of 5940 Å. This means that the half-width of 5940 Å emission band is smaller than that of 5760 Å. Thus, the 5940 Å emission band must be originated from a fast center with a low radioluminescence efficiency. The whole wavelength dependences of decay times $t_{1/e}$ and t_{1/e^2} are given in Figure 3 for 110 K. Obviously there is a characteristic decrease in decay times for wavelengths between 5650 Å and 5850 Å.
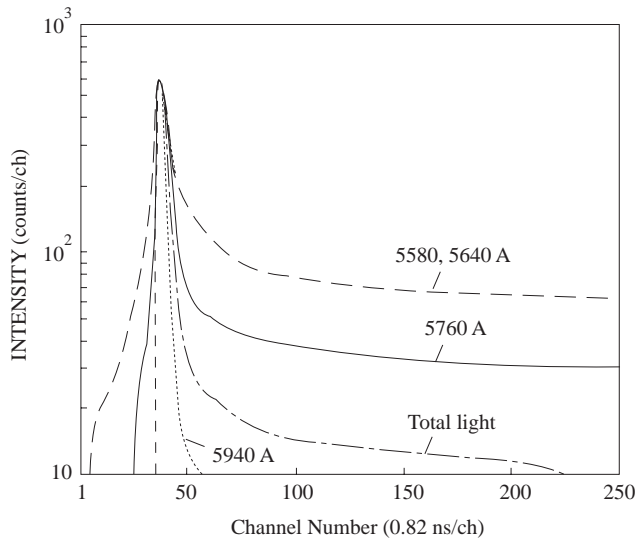
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Figure 2. Radioluminescence decay of CdS(Ag) at 110 K for different emissions.
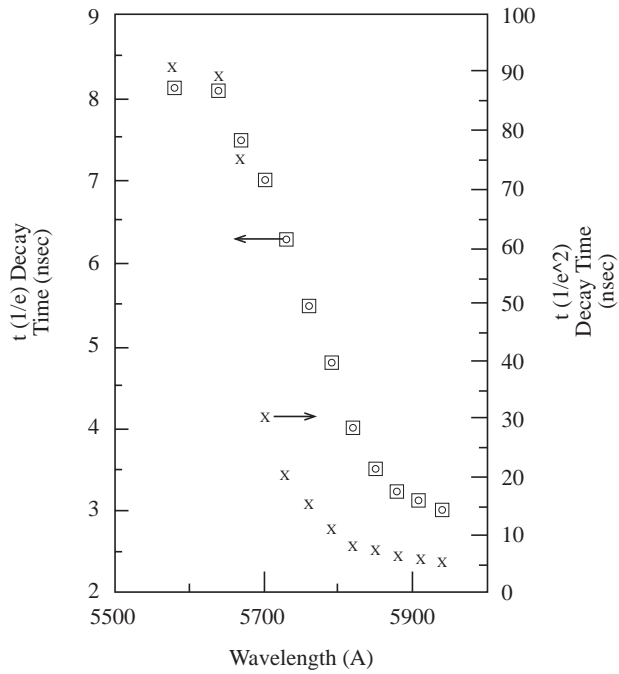

Figure 3. Wavelength dependence of the radioluminescence decay times of CdS(Ag) at 110 K.

The presence of fast and non-exponential decay curves shows that the recombination

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mechanisms are not simple, responsible centers are not isolated, and there might be more than one radioluminescent center. This suggests the existence of donor-acceptor (DA) pair recombination. The broad emission bands observed in Figure 1 also support this conclusion. In general, the characteristic orange emissions in CdS(Ag) were explained in terms of the DA pair recombinations [9, 10, 11].

In Figure 4, the quenching of radioluminescence of CdS(Ag) was measured as its temperature was increased from 90 K to 175 K. As is seen, the 5760 Å emission band quenches rapidly above 120 K, while the 5940 Å emission band persists to about 175 K. Further, we observed that the peak positions and half-widths of both emission bands showed very little variations with temperature. Therefore these emission may not originate from free-to-bound radiative transitions. Above about 175 K, no emission spectra were obtained due to very low level of radioluminescence signals.
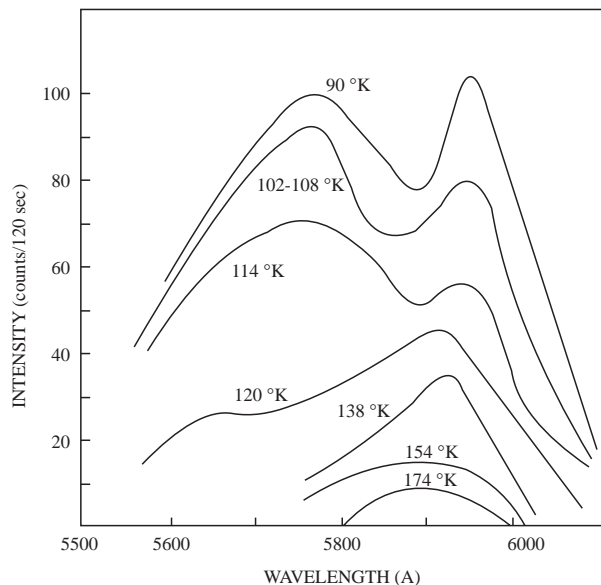

Figure 4. Thermal quenching of radioluminescence spectrum of CdS(Ag).

Using the data (peak values) given in Figure 4, the radioluminescence intensities of the total and two main emission bands were plotted in Figure 5 as a function of reciprocal temperature, $1/T$, in order to perform graphical analysis. It is a common practice to determine the activation energy, E_a, by fitting the data on the thermal quenching of luminescence to and expression of the form

$$I(T) = \frac{I(0)}{1 + C \exp(-E_a/kT)} \qquad (1)$$

where C is a constant, $I(T)$ and $I(0)$ are the luminescent intensities at temperatures T and $0\ K$, respectively, and k is the Boltzmann's constant. The thermal quenching curves,

shown in Figure 5, were found to be smooth for all emissions, i.e., $I(T)$ seemed asymptotic below about 115 K. Since they are stayed nearly constant below this temperature, the asymptotic values of $I(T)$ around 115 K were approximated to $I(0)$. The accuracy of the analysis was slightly affected by the fact that the measurements stopped mostly before this asymptotic $I(0)$ value was reached. Thus, the value of $I(0)$ was varied (with strict limits) so as to optimize the fit in the quenched curves. The $I(0)$ values derived in this way always allowed smooth extrapolation of the experimental data to lower temperatures.
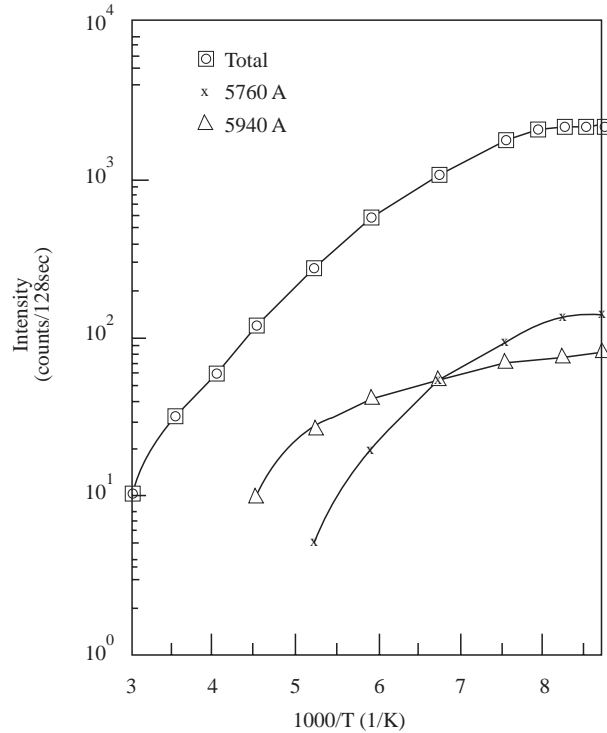

Figure 5. Variation of radioluminescence intensity of total and two main emission bands with temperature in CdS(Ag).

Figure 6 shows a plot of $\ln[I(0)/I(T) - 1]$ vs $1/T$, which gives a straight line. From the slopes of lines, the activation energy values of about $93 meV$, 139 meV and 72.5 meV were determined for the total, 5760 Å and 5940 Å emissions, respectively. The thermal quenching measurements as well as others were repeated many times under almost identical conditions, however, some measurements yielded different values for activation energies in different runs. The average values for all measurements are 97 ± 12.4 meV, 135 ± 35.6 meV and 73.6 ± 13.1 meV for the total, 5760 Å, and 5940 Å emissions, respectively. The differences may be due to the wrong choice of $I(0)$ or spurious variations on $I(T)$ during measurements. The constant term C in equation (1) can be derived from the

intercept of the straight line on the vertical axis. Its corresponding values (averaged over all runs) are $(40 \pm 38) \times 10^3$, $(1653 \pm 1420) \times 10^3$ and (1985 ± 1375) for the total. 5760 Å and 5940 Å emissions, respectively. The interpretation of these intercepts is heavily dependent on the exact quenching mechanism involved in the sample used.
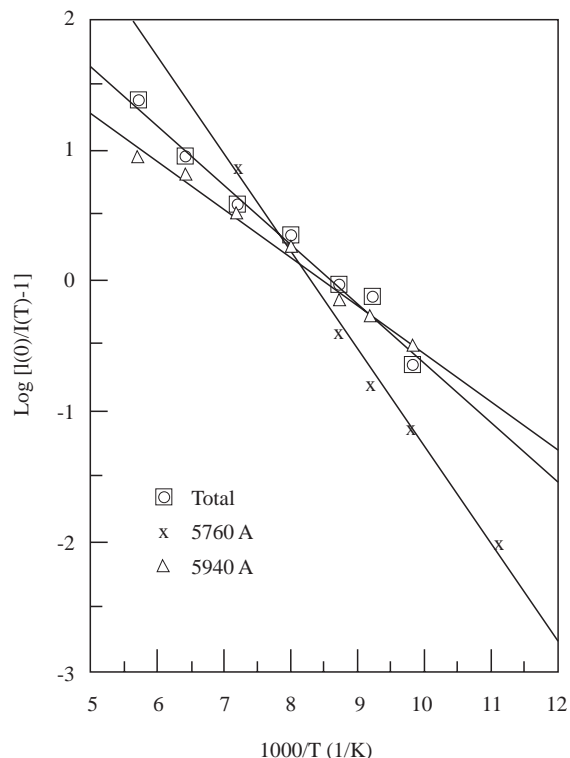

Figure 6. Graphical analysis of the thermal quenching curve $I(T)$ of CdS(Ag).

The temperature dependence of the 5760 Å emission band is found to be similar to that of edge emissions, but its persistence to a slightly higer temperature (120 K) indicates some modification of the acceptor orbitals [21]. This result is also in agreement with the result of Colbov et al [9] who stated that this emission arises from a bound-to-bound transition at distant DA pairs with the silver as the acceptor. The 5940 Å emission band is expected to have a deeper acceptor level than that of the 5760 Å emission band due to its persistence at higher temperature (174 K). However, its calculated value was found shallower (73.6 ± 13.1 meV). Therefore it may not be due to a simple coulombic interaction. Our shallow energy value is also found to be smaller than those of some early results [6, 10, 21]. This may be due to the approximate nature of the several parameters employed.

As is well known, the nature of the DA pair model depends on the presence of the

deep centres in the band gap of the material. The photon energy $E_{h\nu}$ emitted from a DA pair seperated by a distance r is given by [22]

$$E_{h\nu}(r) = E_g - (E_D + E_A) + \frac{e^2}{\epsilon_o r} \tag{2}$$

where ϵ_o is the static dielectric constant, e is the electronic charge, E_g is the band gap energy, and E_D and E_A are the depths of isolated donor and acceptor, respectively.

In CdS(Ag), it is not possible to distinguish whether Ag acts as an acceptor or as a donor. Combining all of the evidence and the deductions for the two main emission bands (5760 Å and 5940 Å), we propose a mechanism containing two seperate DA pair recombination centers, as shown in Figure 7. The depths of the two acceptor levels (due to Ag activation) are suggested as ~ 0.13 eV and ~ 0.07 eV. Making use of equation (2), the ionization energies of the corresponding donor levels were calculated as $E_{5760\text{Å}} = 0.24eV$ and $E_{5940\text{Å}} = 0.36eV$. In this calculation, a band gap energy value of 2.52 eV was used for CdS at 80 K [10], and the Coulombic term in equation (2) was ignored. Unfortunately, the chemical origin of donor levels is not known exactly. So, it is possible to envisage a single donor defect for both emissions (5760 Å and 5940 Å), e.g., a sulphur vacancy, as well as Ag_i interstitial or Cd_i interstitial defects [10, 11]. In that case, the action of the silver incorporation would simply be to encourage the formation of sulphur vacancies.
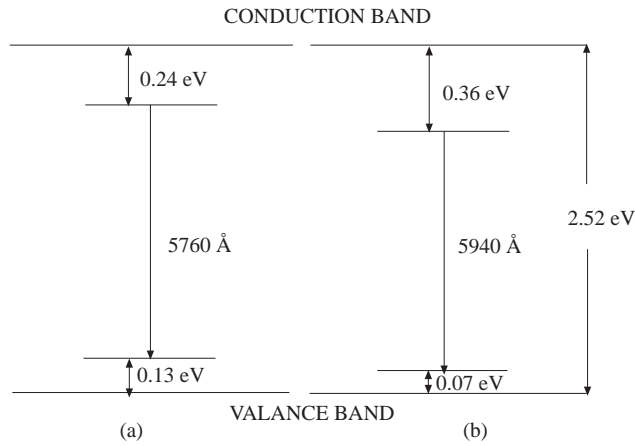

Figure 7. The energy level diagram proposed for (a) 5760 Å and (b) 5940 Å emission bands in CdS(Ag).

4. Conclusion

The radioluminescent properties of CdS(Ag) crystals excited by 5.5 MeV α-particles from an ^{241}Am radioactive source were investigated in detail between room temperature and 80 K, by using single photon counting technique. The two main broad emission

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bands (5760 Å and 5940 Å) were observed. Their $t_{1/e}$ and t_{1/e^2} decay times were determined as fast and non-exponential, i.e., about 6.5 nsec and 15.5 ns for 5760 Å, and, 3.1 nsec and 5.5 ns for 5940 Å, respectively. These decay times were also found to be temperature independent. From the thermal quenching curves, the activation energies of radioluminescent centers which control both emission bands were calculated. We propose two seperate DA pairs consisting of donors with levels at $E_c - 0.24$ eV, $E_c - 0.36$ eV and acceptors at $E_v + 0.13$ eV, $E_v + 0.07$ eV for the 5760 Å and 5940 Å bands respectively (see Figure 7).

Although the experimental system (single-photon counting technique) used here is not sufficient to determine the exact nature of the donor and acceptor states in the energy gap, our results give support to the conclusion that the orange luminescence of CdS(Ag) is most likely due to electron transitions between atoms in DA pairs with levels near corresponding bands. The emission bands associated with such centres should be a superposition of simple subbands due to pairs with different value of interatomic distances between DA pairs. Thus we can report that the DA recombination model for the orange emission bands of CdS(Ag) is in satisfactory agreement with experimental observations.

Acknowledgments

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