The decay kinetics of excitonic luminescence in AgCl crystals

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Abstract. The decay kinetics of the excitonic luminescence observed at 2.5 eV in AgCl after pulsed laser irradiation was measured in wide temperature (10–200 K), time (20 ns–10^{-2} s) and luminescence intensity intervals. It is shown that, at low temperatures, the decay of luminescence is due to the static tunnelling recombination of unidentified shallow electron centres (with a wavefunction radius of about 30 Å) with immobile self-trapped holes. At temperatures above 80 K the relevant luminescence decay starts to differ from that at 10 K and does not obey the usual exponential or second-order kinetics; it was interpreted as diffusion-controlled annihilation within close (geminate) Frenkel pairs of radiation defects. These latter are assumed to be $Ag^{2+}V_c^-$ and interstitial silver atoms Ag_i^0, respectively. Silver atoms are characterized by the 0.15 eV activation energies of hops and a small wavefunction radius of about 1 Å. Thermal quenching of this luminescence is discussed; its activation energy (0.33 eV) corresponds to cation vacancy migration.

1. Introduction

The mechanism and kinetics of photolysis of silver halides is of both fundamental and practical interest. No stable radiation defects are observed below LNT in *pure* AgCl crystals and only silver atom clustering (colloid formation) occurs at room temperature. Unlike alkali halide crystals having the same FCC structure, no evidence of the exciton non-radiative decay into intrinsic lattice defects has been presented so far.

Luminescence of AgCl crystals has been investigated in detail [1–7]. It reveals a broad peak at 2.5 eV consisting of a superposition of intrinsic exciton emission (with two lifetimes of about 1.5 ns and 10 μs [8]) and a long non-exponential tail which was ascribed earlier to donor–acceptor (tunnelling) recombination [3,7,9]. Since luminescent spectroscopy is very sensitive and efficient in defect studies, in this paper we continue these luminescence studies, focusing our attention on time-resolved luminescence from pure AgCl crystals measured in wide temperature (10–200 K) and time (10 ns–10^{-2} s) intervals, in order to shed more light on the nature of primary short-lived radiation defects in silver halides.

2. Experimental details: technique and results

The specimens of AgCl investigated here were grown from specially purified powders with cation impurity contents smaller than 10^{-5} wt%. It is probable that some molecular impurities are adsorbed by specimens during their preparation and storage; IR spectral bands associated with H_2O and SO_4^{2-} molecular impurities measured for some samples indeed increase in time. This can easily happen since the specimens were annealed for a long time at 600 K in open air.

A pulsed nitrogen laser ($hv = 3.67$ eV and a pulse duration of 8 ns) was used for luminescence excitation. The luminescence decay was measured after pulsed excitation in the time range 10 ns–10 ms.

Two luminescence-detecting systems were used:

(i) a time-correlated single-photon-counting system whose time resolution could be set to 10, 40 and 160 ns;

(ii) photon counting in a gate (multichannel analyser); the gate width can be set to 1, 10 and 100 μs.

The system consists of 127 channels; so the shortest decay recording time ranges between 0 and 1270 ns, whereas the longest decay recording time ranges between 100 and 12 700 μs. The decay kinetics were accumulated in 10^5 excitation cycles. Both detection systems are synchronized with the laser light pulses; so we have very well defined zero time, allowing us to combine the luminescence decay kinetics measured in the different time ranges.

Excitonic decay kinetics at four characteristic temperatures (10, 55, 80 and 120 K) are presented in figure 1. Figure 2 shows the luminescence intensity versus the temperature. It is quenched efficiently above 200 K with an activation energy of 0.33 eV. Theoretical interpretation of these results is discussed in the next section.

3. Theory

As is well known, self-trapped holes (STHs) and excitons in AgCl are immobile below 30 K [2, 3]. Therefore, kinetics observed at 10 K (figure 1) arise owing to the static tunnelling recombination of immobile electron–hole defects, which has been confirmed experimentally [7, 9]. We assume that the spatial distribution within these pairs is the exponential function of the relative distance, r:

$$f(r) = (1/b) \exp(-r/b) \tag{1}$$

where b is half the mean distance between defects.

The luminescence intensity is [10]

$$I(t) = \int_0^\infty W(r) f(r) \exp[-W(r)t] \, dr. \tag{2}$$

From equation (2) the probability of the tunnelling recombination is

$$W(r) = W_0 \exp(-r/a) \tag{3a}$$

where a is half the Bohr radius of the wavefunction of the electron centre and W_0 is a constant. For the alternative annihilation mechanism of defect disappearance,

$$W(r) = W_0 \Theta(r - R_0) \tag{3b}$$

where Θ is the Heaviside step function and R_0 the annihilation radius. At relatively long times, ($W_0 t \gg 1$), the defect concentration decays as [10]
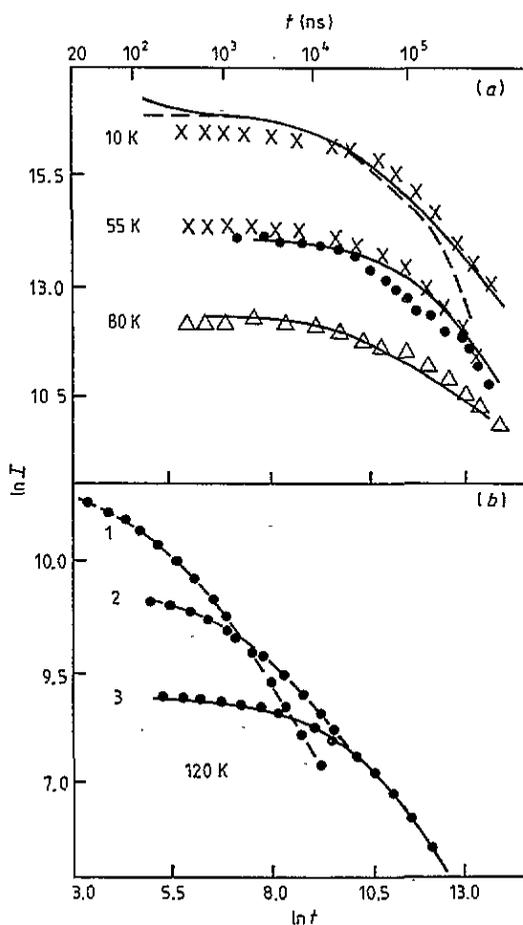
$$n(t)/n_0 = \Gamma(1 + a/b)(W_0 t)^{-a/b} \tag{4}$$

Figure 1. (*a*) The kinetics of the excitonic luminescence decay at the three characteristic temperatures (10, 55 and 80 K): ———, experimental data; – – –, curve for 10 K showing the results for the static tunnelling recombination for deep electron centres (half the wavefunction Bohr radius $a = 0.5$ Å) well correlated with acceptors (1NN + 2NN, i.e. 2.49 Å and 4.78 Å); ×, data for $T = 10$ and 55 K corresponding to another extreme case of shallow donors ($a = 15$ Å) with an almost random distribution with respect to acceptors ($b = 75$ Å; see equation (1)); ●, data for 55 K showing the kinetics controlled by diffusion and annihilation; △, data for 80 K showing diffusion-controlled annihilation of well correlated defects (1NN + 2NN) with an annihilation radius $R_0 = 1$ Å, $E = 0.15$ eV, $D_0 = 1.5 \times 10^{13}$ Å^2 s^{-1} and $\alpha = 0.5$ eV Å^3 [12]. (*b*) The calculated decay kinetics at 120 K for three activation energies of Ag_i^0 hops: curve 1, 0.15 eV; curve 2, 0.175 eV; curve 3, 0.20 eV. The experimental curve almost coincides with curve 3.

where Γ is Euler's gamma function. Equation (4) results in the asymptotic law of luminescence decay:

$$I(t) = -\mathrm{d}n(t)/\mathrm{d}t = t^{-(1+a/b)}. \tag{5}$$

For alkali halides, typical values of the ratio a/b are about 0.1. In turn, for a random defect distribution the decay is known to be slower [10]:
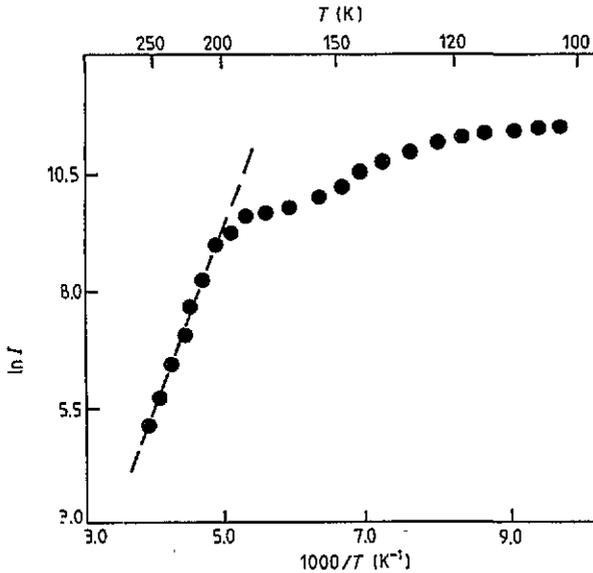
$$I(t) \propto [\ln^2(W_0 t)]/t. \tag{6}$$

Figure 2. Thermal quenching of the 2.5 eV luminescence band.

The conclusion could be drawn from figure 1(a) ($T = 10$ K) that equation (5) holds at $t > 3 \times 10^{-3}$ s, giving the estimate of W_0 as about 3×10^4 s^{-1}, which is close to the typical values for donor–acceptor pairs in semiconductors. Fitting of the whole kinetics given by equation (2) to the experimental curve at 10 K yields the parameters $a \simeq 15$ Å and $b \simeq 75$ Å, demonstrating that we deal with shallow donors and a very broad defect distribution over relative distances. It is in good agreement with previous low-temperature ODMR results [7, 11] and decay kinetics studies [9].

For comparison the kinetics for deep donors ($a = 1$ Å) spatially strongly correlated with acceptors is also shown in figure 1(a) by a broken curve. It gives worse agreement with the experimental curve at 10 K, considerably deviating from it at $t > 10^{-4}$ s.

At the temperature when defects become mobile, the relative distribution of electron–hole defects is described by their joint density $Y(r, t)$ obeying the following equation [10, 12]:

$$\frac{\partial Y(r, t)}{\partial t} = D\nabla \cdot \left(\nabla Y(r, t) + \frac{Y(r, t)}{kT}\nabla U(r) \right) - W(r)Y(r, t) \qquad (7)$$

where $D = D_0 \exp(-E/kt)$ is the relative diffusion coefficient, E is the activation energy for diffusion and $U(r)$ is the energy of elastic defect interaction as a function of the interdefect distance [12–14]:

$$U(r) = -\alpha/r^3, \qquad (8)$$

where α is a constant. The initial condition is $Y(r, 0) = f(r)$.

The diffusion-controlled luminescence decay is governed by the equation

$$I(t) \propto \int_0^\infty W(r)Y(r, t)\, dr. \qquad (9)$$

For the initial random defect distribution we have asymptotically (as $n_A = n_B = n$ and $t \to \infty$) for both annihilation and tunnelling recombination [10]

$$n(t) \sim t^{-1} \qquad I(t) \propto t^{-2}. \qquad (10)$$

At the intermediate temperature (55 K) the kinetics are still better approximated by the static (on a given time scale) tunnelling recombination of almost randomly distributed shallow donors with acceptors (as at 10 K) rather than by the diffusion-controlled annihilation of well correlated defects.

However, at the higher temperature (80 K) the kinetics are already described well in terms of the diffusion-controlled annihilation of closely spaced (first-nearest-neighbour (1NN) and second-nearest-neighbour (2NN)) defects. Strong initial correlation within these pairs is also well seen from the complicated decay law which does not obey equation (10). This is in line with previous studies of primary radiation defects in both silver halides [6, 12] and alkali halides [14–16].

Fitting of equations (7)–(9) to the experimental kinetics at 80 K yields the following numerical parameters: diffusion energy $E = 0.15$ eV; $D_0 = 1.5 \times 10^{13}$ Å s^{-1}; elastic interaction parameter $\alpha \leqslant 0.1$ eV Å^3. (For more details of the methodology of parameter fitting see [12].) This means, in particular, that (unlike alkali halides [14]) elastic interaction of primary defects is negligibly small here. This agrees with our recent idea [6, 12] that the donor is an interstitial silver atom which does not distort the surrounding lattice considerably. The diffusion activation energy of 0.15 eV also supports the idea of a deep well localized defect rather than a shallow donor centre. This value exceeds considerably the relevant activation energy of migration of the interstitial silver ions (0.05 eV) via an interstitialcy mechanism [17].

Our parallel studies of short-lived absorption bands [6, 12] have revealed a novel defect arising at a temperature close to LNT whose absorption peaks at $E = 2.7$ eV; it was attributed by us to the interstitial silver atom Ag_i^0. From this absorption energy E, one can estimate easily the Bohr radius of the wavefunction of the defect to be $\varphi = \exp(-r/a)$, where [18]

$$a \simeq 1/(8/3E)^{1/2} \simeq 1.1 \text{ Å}. \tag{11}$$

This value is close to that observed for the main deep electron defects (F centres in KCl) and gives strong support to the theoretical calculations, arguing that Ag_i^0 defects are deep well localized centres rather than shallow defects, as was commonly accepted earlier (see discussion in section 6.3 of [12]).

Finally figure 1(b) shows the results of the theoretical fitting to the experimental kinetics at the high temperature of 120 K. The best results are obtained if we also vary the activation energy for Ag_i^0 hops; the optimal value turns out to be 0.20 eV. A possible explanation why it is higher than at lower temperatures (0.15 eV) is that it is the effective value modified by the retrapping of very mobile silver atoms by impurities. Using the theory [10], one can find easily that this could happen for traps with the binding energy $E_B = 0.23$ eV (i.e. the delocalization energy $E_D = E_B + E = 0.38$ eV) which are present with a concentration $C_T = 10^{16}$ cm^{-3}.

4. Discussion

The mechanism of short-lived luminescence observed near LNT in mixed silver halides whose last stage involves radiative exciton emission near a cation vacancy $(Ag^+V_c)^*$ has been suggested by us recently [6, 12]. The present study of the temperature dependence of exciton luminescence kinetics has demonstrated that this recombination process is quite complicated and consists of several elementary stages of electronic excitation relaxations.

These stages can be summarized in the following way. For the decay kinetics of the excitonic luminescence at low temperatures ($T \geqslant 10$ K) the best fitting of the experimental

curve and theoretical calculation gives the model of tunnelling recombination. Its analysis reveals an almost random distribution of immobile donors and acceptors. The former are shallow centres whose nature is not clear and, in particular, whether they are impurity and/or radiation induced. (In the past the generally accepted point of view was that these are interstitial Ag_i^0.) The hole component of the donor–acceptor pair is either Ag^{2+} (the STH becomes mobile at $T > 35$ K [8]) or a $Ag^{2+}V_c^-$ centre (whose low-temperature thermal bleaching starts only at 70 K [19]).

The temperature range $80 \text{ K} \leqslant T \leqslant 150 \text{ K}$ is well described theoretically in terms of diffusion-controlled recombination (DCR) within Frenkel pairs of complementary defects, presumably Ag_i^0 and $Ag^{2+}V_c^-$—the idea presented for the first time by us in [6, 12]. These defects are spatially well correlated (1NN + 2NN), and the deep donor centres involved have a wavefunction radius of only about 1 Å. We assume that recombination occurs in two stages: firstly electron release to the conduction band from Ag_i^0 either trapped by V_c^- or strongly perturbed by the vacancy; secondly trapping of this electron on Ag^{2+}, resulting in the formation of a self-trapped exciton (STE) and its radiative annihilation.

Finally, at intermediate temperatures ($30 \text{ K} \leqslant T \leqslant 70 \text{ K}$), the tunnelling recombination within randomly distributed donor–acceptor pairs occurs but it is not certain that the diffusion-controlled process takes place too.

An important conclusion suggested from our results of decay kinetics investigations is that STE luminescence is the last stage of different processes and its description depends on temperature.

The energy position of this excitonic luminescence band centred at 2.5 eV varies very slightly with the temperature, whereas its half-width increases from 0.32 to 0.38 eV, as the temperature increases from 10 to 80 K, respectively. It is well known [4] that the temperatures of quenching of this luminescence in pure samples and those doped with M^{2+} impurities differ considerably. Combined with the constant spectral composition of the excitonic luminescence, this means that intrinsic emission occurs from the same centre but having a different surrounding environment, thus affecting the subtle balance between the probabilities of radiative and non-radiative transitions.

Our investigations of STE luminescence thermal quenching shows that it has typically a many-stage character, dependent strongly on the purity of specimens. It obeys the Mott law only at high temperatures ($T > 200$ K). In our opinion, the relevant activation energy (0.33 eV in our paper and 0.36 eV [20] for this high-temperature stage) argues strongly for the intrinsic mechanism of the cation vacancy migration.

As is known, the ESR studies of $Ag^{2+}V_c^-$ [19] reveal the two stages of thermal quenching, at 70 and 110 K, observed for the two different positions of V_c^- with respect to the Ag^{2+} ion. In the most stable complex centre, V_c^- is a 1NN with respect to the Ag^{2+} centre; the relevant binding energy was estimated to be 0.37 eV [19]—which is very close to the quenching activation energy observed by us (0.33 eV; see section 2 above), as well as the activation energy for V_c^- migration (0.35 eV [17, 21]).

In particular, V_c^- perturbation of $(Ag^+)^*$ makes the luminescence observable at $T \simeq 200$ K whereas the luminescence of the isolated $(Ag^+)^*$ centre (exciton) is quenched much earlier. Note that the decay in the intensity of the former intrinsic luminescence probably might occur not only because of the intrinsic quenching but also as a result of the thermal dissociation of the $Ag^{2+}V_c^-$ complex centre, or for another reason.

The considerable gap in the temperatures of ESR signal disappearance described in [19] and of the luminescence quenching accompanied by very similar activation energies observed for these processes can be explained in the following way.

(i) In the luminescence studies, $Ag^{2+}V_c^-$ is formed as a defect complementary to Ag_i^0 [12]; its presence in the vicinity of the latter increases its thermal stability.

(ii) The thermal annealing of the centre begins at about 100 K but, since the luminescence is produced by short-lived centres, this centre is observed up to 200 K.

(iii) At $T \simeq 100$ K the migration (rather than dissociation) of $Ag^{2+}V_c^-$ very probably happens, and it is the activation energy for V_c^- migration which mainly controls this process.

Finally, above 200 K the DCR efficiency is reduced owing to mixing of primary Frenkel pairs and thus the probability of the competing process of the Ag_i^0 aggregation increases; silver cluster formation becomes important. Together with this process, the aggregate centres containing holes and V_c^- are formed too (analogously to large F-centre aggregates in alkali halides [22]). Annealing of these aggregate centres means that the samples need to be kept at high temperatures for a long time, probably because of a very slow AgCl structure ordering process. Both the slow ordering and the existence of such aggregates just mentioned are supported by a number of experimental studies of the induced absorption at the fundamental edge and restoration of the uniform halogen distribution in mixed silver halides [23]. As was discussed above, the silver colloid formation process may occur without thermal dissociation of the $Ag^{2+}V_c^-$ complex centre.

Analysis of our own experiments on luminescence decay kinetics and our former experiments on transient absorption [6] provide evidence of the complicated process of elementary excitation relaxation in silver halides. In the temperature range 10–80 K, trapping and self-trapping of electrons, holes and excitons take place. At 80 K and higher temperatures, elementary excitation non-radiative decay of primary Frenkel defects is important. In the temperature region 80–200 K, mainly DCR of primary defects occurs; above 200 K a thermostimulated process led to the aggregation of defects. The formation of defect aggregates and/or silver colloids in our experiments was not observed directly; it was deduced from the change in luminescence decay kinetics, showing the mixing of Frenkel pairs. From the existing literature it is known that silver colloid formation occurs at room temperature whereas at 80 K it does not. Thus we obtain the model of relaxation of elementary excitations in AgCl, which is schematically shown in figure 3 (with some modifications it is valid also for mixed silver hallides, and—excluding hole self-trapping— even for pure AgBr) and can be summarized as follows.

High-energy excitation creates electron–hole pairs in AgCl. The existence of free excitons is also possible, in principle, but its resonance luminescence ($h\nu_1$) in AgCl experimentally was not observed [5, 16]. The relaxation of high-energy excitations may result in STE or bound exciton formation (e.g. in the $AgBr_{1-x}Cl_x$ system), whose radiative annihilation reveals the luminescence energy $h\nu_2$ (STE) and $h\nu_3$ (bound exciton), respectively. The last process is not shown in figure 3.

At LHT, radiation-induced electrons are trapped at shallow levels whereas holes become self-trapped. The recombination kinetics are described as static tunnelling (process 1 in figure 3) [7, 11]. This is true up to $T \leqslant 80$ K. At higher temperatures the non-radiative exciton decay into Frenkel pairs $\{Ag^{2+}V_c^- - Ag_i^0\}$ (process 2) becomes increasingly efficient; the recombination of these correlated pairs turns out to be diffusion controlled. The suggested scheme in figure 3 also explains the colloid formation process in silver halide.

5. Conclusion

In conclusion, we would like to stress the necessity of further careful studies of a novel radiation-induced intrinsic defect in AgCl (an interstitial Ag_i^0 atom, in our opinion).
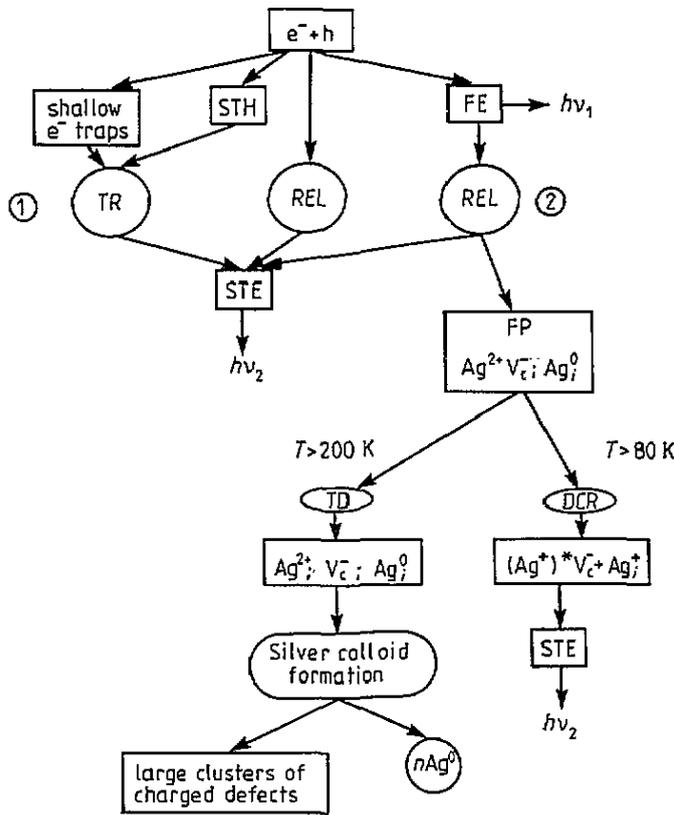
Figure 3. Schematic diagram of the radiation-induced defect processes in AgCl: $h\nu_1$, the resonant luminescence energy of free excitons; $h\nu_2$, exciton annihilation energy in the regular lattice; e^-, electrons; h holes; STE, self-trapped exciton; STH, self-trapped hole; FE, free exciton; FP, Frenkel pair of defects; REL, relaxation process; TR, tunnelling recombination of electron and hole defects; TD, thermal dissociation (of the $Ag^{2+}V_c^-$ complex); DCR, diffusion-controlled recombination.

In particular, the temperature dependence of its generation efficiency, a reason for its appearance only at relatively high temperatures (around LNT) and its relation to the primary low-temperature shallow donors (earlier identified as Ag_i^0) should be studied.

Also theoretical as well as experimental studies of the possibility and actual mechanism of one-centre exciton decay into lattice defects ($Ag^{2+}V_c$ and Ag_i^0 in our opinion), remain of great importance.

Acknowledgments

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