

## Low-temperature donor-acceptor recombination in silver halides

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(Received 19 November 1984)

The time and wavelength evolution of the optical emission from AgCl and AgBr at low temperature ( $\sim 4$  K) has been investigated. These data characterize the emission from AgCl ( $\lambda_{\text{max}} = 500$  nm) as partially due to donor-acceptor recombination and from AgBr ( $\lambda_{\text{max}} = 580$  nm) as wholly due to donor-acceptor recombination. These conclusions are supported by optically detected magnetic resonance data and other spectroscopic information, which suggest that the donors are interstitial silver ions or substitutional divalent-cation impurities and that the acceptor in AgCl is a self-trapped hole.

### INTRODUCTION

The low-temperature photophysics of silver halides is of fundamental as well as practical interest. Near ambient temperature, band-gap irradiation of small silver halide crystals causes the formation of silver clusters.<sup>1</sup> Below  $\sim 60$  K these processes are suppressed, and most of the light absorbed by the sample is reemitted at longer wavelengths.<sup>2,3</sup> The nature of these efficient emission processes is the subject of this investigation.

Numerous investigations of the emission from AgCl and AgBr have been published, and much of this work has been reviewed.<sup>3</sup> AgCl has a broad emission band peaking at  $\sim 500$  nm. AgBr has two emission bands—one at 495 nm, which is associated with residual iodide impurities, and a broadband at  $\sim 580$  nm. In addition, weak, structured emission is observed near the band edge in both systems.<sup>4,5</sup> This emission has been identified as a band-to-band transition in AgBr.<sup>4</sup>

The data in this paper will be interpreted in terms of the donor-acceptor model of radiative recombination.<sup>6</sup> In this model electrons are weakly trapped in large orbits at donor sites, and the holes are trapped at acceptor sites. Radiative recombination occurs by interactions or tunneling between donor-acceptor pairs, the closer pairs recombining more rapidly. If there is a Coulomb interaction between donors and acceptors, the emission wavelength will evolve in time. This evolution reflects both the distance dependence of the Coulomb term and the decay rate.

Time and wavelength evolution of the emission and optically detected magnetic resonance (ODMR) spectra have been used previously to characterize a 530-nm emission from  $\text{AgBr}_{0.97}\text{I}_{0.03}$  as due to donor-acceptor recombination.<sup>7</sup> This work provides a useful basis on which to interpret the emission from AgCl and AgBr.

### EXPERIMENTAL

AgCl and AgBr were precipitated with distilled HCl and HBr from an aqueous solution of  $\text{AgNO}_3$ , synthesized from 9999.99% pure silver shot and distilled  $\text{HNO}_3$ . Water was multiply distilled and deionized. The samples were precipitated and handled in the dark or under red light. Crystals were grown from the washed, dried precip-

itate by conventional Bridgman techniques. All samples were analyzed for impurities by standard emission-spectrographic and/or neutron-activation techniques.

A pulsed  $\text{N}_2$  laser was used to excite samples with 337.1-nm radiation. The laser pulses had a width (full width at half maximum) of  $< 0.5$  ns and energies of 3–5  $\mu\text{J}/\text{pulse}$ . An ultraviolet-cutoff filter, a compact monochromator, and a red-sensitive photomultiplier tube (RCA 4832) were used to monitor the emission. The spectral resolution was  $\sim 3$  nm. The photomultiplier response was fed into a Tektronix 7704A digital processing oscilloscope for signal averaging and graphics display. All emission-decay curves presented here are the average of at least 32 transients. The ODMR apparatus has been described.<sup>8</sup>

Temperature was varied (10–200 K) with a CTI-Cryogenics helium refrigerator. Measurements at 4.2 K were in a conventional glass cryostat with the sample immersed in liquid helium.

### RESULTS

Figures 1 and 2 show the time and wavelength evolution of the emission spectra from AgCl and AgBr at 4.2 K after pulsed excitation. These spectra show no shifts in wavelength as a function of time. This is in contrast to the observations on the  $\text{AgBr}_{0.97}\text{I}_{0.03}$  system,<sup>7</sup> where a 15-nm red shift was observed at long times. Figures 1 and 2 also show log-log plots of the emission decay after pulsed excitation for AgCl and AgBr. The dashed lines are theoretical decay curves for donor-acceptor emission (see below). Semilog plots of the same data (not shown) reveal the distinctly nonexponential nature of the decay. As the sample temperature is increased, the emission decays more rapidly and the decay becomes more nearly exponential. Activation energies for emission quenching were obtained from Arrhenius plots of the initial decay rates, using the linear part of the curve ( $T \geq 100$  K), assuming that

$$K = A \exp(-E_a/kT), \quad (1)$$

where  $K$  is the first-order rate constant,  $A$  is the frequency factor, and  $E_a$  is the activation energy. For AgBr, the reciprocal of the emission intensity was used to follow the quenching dynamics to high temperature, as the signal at 580 nm is weak. Table I gives the results of these analy-

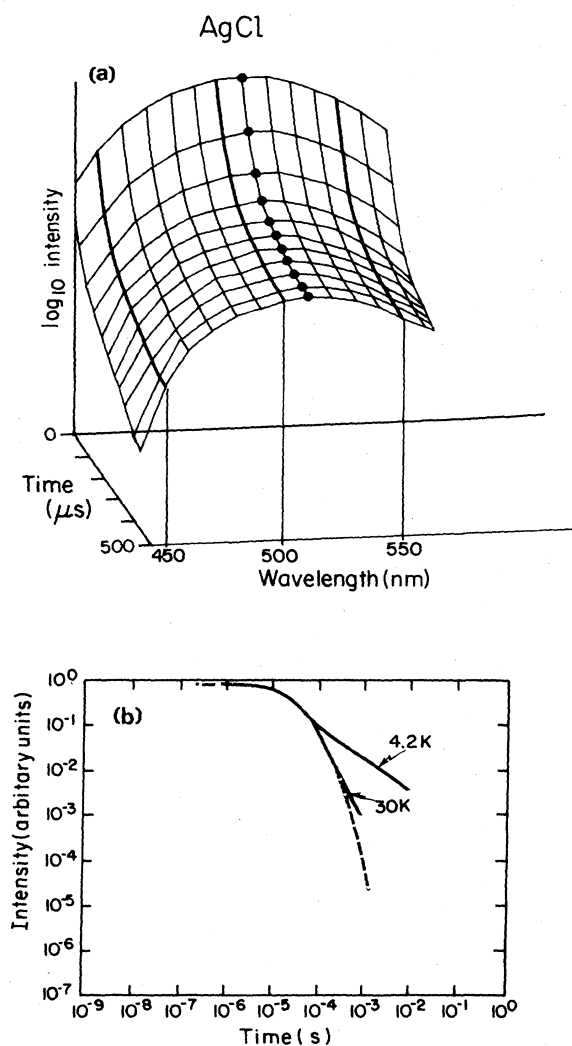


FIG. 1. (a) Time and wavelength evolution of the emission from AgCl at 4.2 K. The dots denote the emission peak. (b) Log-log plot of the emission decay monitored at  $\sim 500$  nm at 4.2 and 30 K. Dashed line is the theoretical<sup>16</sup> decay curve for  $10^{20}$   $\text{cm}^{-3}$  donors or acceptors.

ses. The values of  $E_a$  given in Table I are close to the binding energies expected for an electron in a Coulomb potential in these materials (65 meV for AgCl and 35 meV for AgBr).

#### DISCUSSION AND ODMR RESULTS

The interpretation of the data given in Figs. 1 and 2 and Table I is facilitated by considering the published

TABLE I. Arrhenius parameters for AgCl and AgBr.

Substance	$A$ ( $\text{s}^{-1}$ )	$E_a$ (meV)
AgCl	$10^5$	$65 \pm 12$
AgBr	$10^9$	$40 \pm 5$
$\text{AgBr}_{0.97}\text{I}_{0.03}^a$	$(3.5 \pm 1) \times 10^7$	$40 \pm 8$

<sup>a</sup>Data taken from Ref. 7.

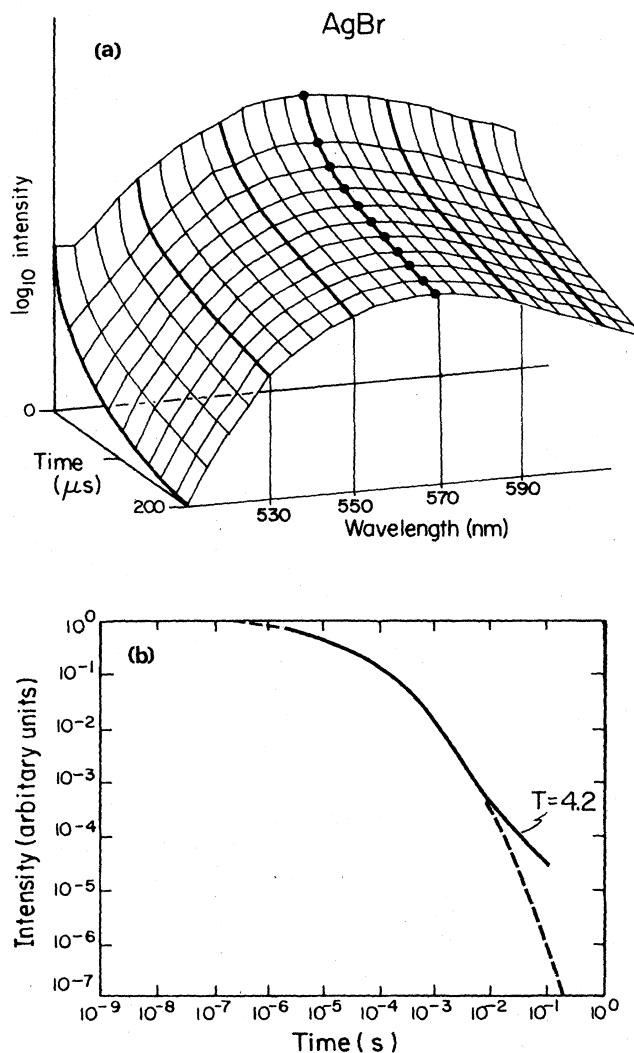


FIG. 2. (a) Time and wavelength evolution of the emission from AgBr at 4.2 K. The dots denote the emission peak. (b) Log-log plot of the emission decay monitored at  $\sim 580$  nm and at 4.2 K. Dashed line is the theoretical decay curve for  $10^{18}$   $\text{cm}^{-3}$  donors or acceptors.

ODMR studies of AgCl (Refs. 8–10) and AgBr (Refs. 10–12). The ODMR spectrum of AgCl is complex, with resonances from as many as six species.  $\text{AgCl}_6^{4-}$ , the self-trapped hole (STH), has been observed. Two self-trapped exciton (STE) species that consist of electrons bound weakly to STH's occur, one containing a bromide (impurity) in the first shell of the STH. Three electron species have also been identified. One has a  $g$  value close to that of a conduction-band electron, but it is probably associated with a shallow trap at low temperature ( $\sim 4$  K).<sup>7</sup> The other electron resonances come from a tetragonally distorted center and its undistorted analog. The existence of these centers is dependent on magnetic field,<sup>8</sup> and they are not observed at low magnetic fields ( $\sim 3$  kG). This is illustrated in the ODMR spectrum of AgCl (Fig. 3), where only three species are observed. The  $g = 1.88$  resonance at  $\sim 3.46$  kG is from an electron trapped at a

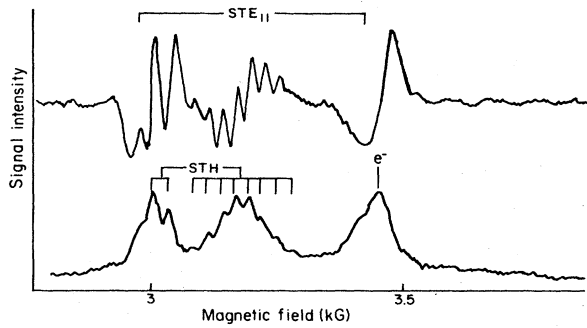


FIG. 3. ODMR spectrum of AgCl at 4.2 K.  $\nu=9.050$  GHz. The upper spectrum was obtained with magnetic-field modulation, the lower with microwave modulation.  $STE_{||}$  denotes the parallel component of the STE.

Coulomb center, the doublet at  $\sim 3.02$  kG and the octet at  $\sim 3.18$  kG are the parallel and perpendicular components of the STH, and the doublet centered at  $\sim 3.21$  kG is the parallel component of the STE.<sup>8-10</sup> This simple low-field ODMR spectrum implies that the zero-field radiative recombination will not be as complex as suggested by the high-field ODMR data.

The radiative recombination process in AgCl is defined by the information in Fig. 1 and the ODMR data in the context of a donor-acceptor model.<sup>6</sup> The "acceptor" is a lattice silver ion, which self-traps holes. There are several donor species at high fields, but at zero field the only one remaining appears to be a Coulomb center (interstitial silver ion or a substitutional divalent cation), which binds an electron in a large orbit.<sup>13-15</sup> Large variations in donor-trap depth can be ruled out. The emission-wavelength dependence of the uncoupled spins observed in the ODMR spectra is the same ( $\lambda_{\max}=510$  nm).<sup>8</sup> The 65-meV activation energy given in Table I may include a contribution from exciton species but nonetheless is com-

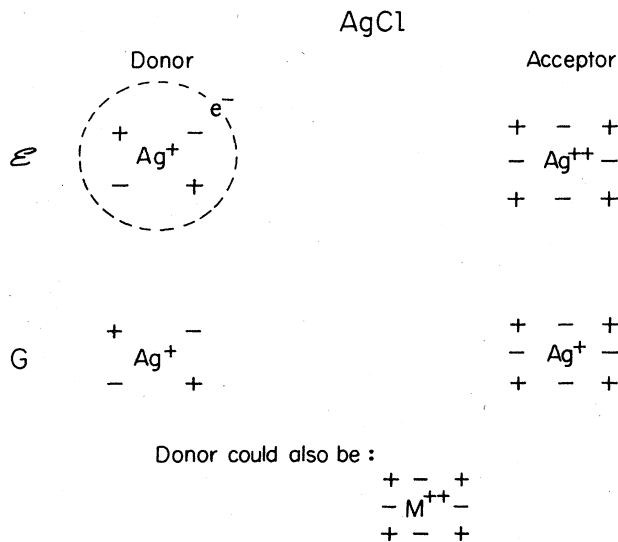


FIG. 4. AgCl donor and acceptor species in their ground (G) and excited ( $\mathcal{E}$ ) states.

parable to the  $\sim 48$  meV calculated from spectroscopic data<sup>13-15</sup> for the binding energy of an electron to a Coulomb center.

Figure 4 is a diagram of the donor and acceptor species in their ground and excited states. There is no change in Coulomb interaction between the donor and acceptor upon excitation, with the electron and hole species identified from ODMR data (see below). Thus no wavelength shift with time is expected, in accordance with the observation in Fig. 1. The log-log plot of the emission decay is fit reasonably well by the theoretical decay curve at short times in the 4.2-K curve and over the full 30-K curve for a donor-acceptor system—with  $10^{20}$  cm<sup>-3</sup> donors or acceptors.<sup>6</sup> The numbers derived from this fit may be in error, as the system was not shown to be saturated at the intensities used in this work. At very low temperatures ( $< 10$  K) there are two self-trapped excitons, which should have exponential decays, that contribute to the emission. These excitons may become unstable<sup>8</sup> above  $\sim 10$  K and may be responsible for changes in the decay-curve shape between 4 and 30 K. The long-time component of the emission observed at 4.2 K (Fig. 1) may be due to additional shallow impurities.

The ODMR spectrum of AgBr consists of four resonances. The highest-field resonance occurs at a  $g$  value close to that of a conduction-band electron. This electron is associated with a donor center at low temperatures. The lowest-field resonance was assigned to a free-hole transition, but recent investigations by Stolz *et al.* suggest that this may be a trapped hole.<sup>16</sup> The two intermediate resonances are thought to be an electron and a hole resonance.<sup>7</sup>

The luminescence of AgBr is similar to that of AgCl, in that the emission wavelength does not shift with time. This implies that the Coulomb interactions between the

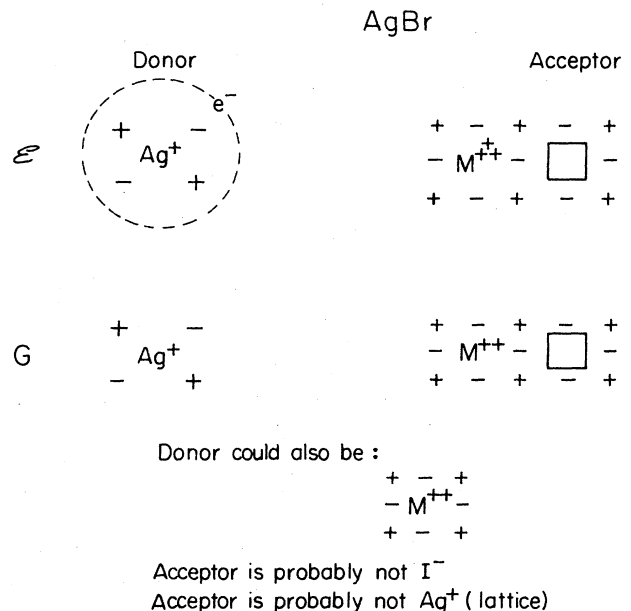


FIG. 5. AgBr donor and a possible acceptor species in their ground and excited states.

donor and the acceptor do not change upon excitation. This restricts the nature of the trap sites. The donors are interstitial silver ions or divalent-cation impurities. This is supported by the activation energy given in Table I and other spectroscopic data,<sup>13-15</sup> which give an electron binding energy of  $\sim 30$  meV from the far-infrared  $1s-2p$  transition of these hydrogenic centers. The acceptor species have been observed but not identified in AgBr. One possibility, shown in Fig. 5, is a vacancy-compensated divalent cation, which can trap a hole. Several possible acceptors, however, can be ruled out. Holes trapped at silver-ion vacancies are ruled out on the basis of charge considerations; emission wavelength did not shift with time. Self-trapped holes can be eliminated as an acceptor species in AgBr because holes are known not to self-trap in AgBr.<sup>17,18</sup> Single iodide ions trap holes but can also be ruled out as an acceptor species on the basis of their hole binding energy.<sup>19</sup> They bind holes too weakly to account for the large shift of the 580-nm emission from the band edge (see below). The concentration of multiple iodide centers at iodide impurity levels of  $\sim 1$  molar ppm is exceedingly small.

Characterization of the emission from AgCl and AgBr as donor-acceptor (DA) recombination radiation implies that the emission energy is given by

$$E_{DA} = E_g - (E_D + E_A) + E_C, \quad (2)$$

where  $E_g$  is the energy of the band gap (2.681 eV for AgBr and 3.237 eV for AgCl),<sup>4</sup>  $E_D$  and  $E_A$  are the donor and acceptor binding energies, and the last term is the difference in Coulomb energy of the pair<sup>6,20</sup> in their ground and excited states. If the transition from excited to ground state of the pair results in no net change in the Coulomb energy, as proposed for AgCl and AgBr, then this term is zero. The pair-distance dependence of the emission is removed, giving rise to an emission that does not shift in wavelength with time. The energy of the lead-

TABLE II. Estimates of the donor and acceptor binding energies in AgCl and AgBr.

	$E_g$ (eV)	$E_{DA}$ (eV)	$E_D + E_A$ (meV)	$E_D$ (meV) <sup>a</sup>	$E_A$ (meV)
AgCl	3.237	$2.770 \pm 0.020$	$470 \pm 20$	$65 \pm 12$	$405 \pm 25$
AgBr	2.681	$2.310 \pm 0.050$	$370 \pm 50$	$40 \pm 5$	$330 \pm 50$
AgBr <sub>0.97</sub> I <sub>0.03</sub> <sup>b</sup>	$2.560^c$	$2.505 \pm 0.020$	$55 \pm 20$	$28 \pm 2^d$	$27 \pm 20$

<sup>a</sup>Data taken from Table I.

<sup>b</sup>Data taken from Ref. 7.

<sup>c</sup> $E_g$  differs from the value in Ref. 7 and represents recent measurements.

<sup>d</sup>Estimated from Refs. 12-14.

ing edge of the emission, the data in Table I, and Eq. (2) can be used to estimate the combined donor-acceptor binding energies and the adiabatic acceptor-trap depth. These data are given in Table II.

The binding energies derived for the acceptors in AgCl and AgBr are in reasonable agreement with the range of data obtained from infrared transient absorption measurements.<sup>18,21</sup> The data given in Table II indicate that holes are deeply trapped in AgCl and AgBr, yet they are not often observed above  $\sim 60$  K. Their disappearance, however, is sometimes observed with a parallel change in some electron species, so that their detection may be strongly dependent on the stability of the trapped electrons.<sup>22</sup>

## CONCLUSIONS

The 500-nm emission from AgCl and the 580-nm emission from AgBr can be characterized as due to donor-acceptor radiative recombination. The donors appear to be interstitial silver ions or substitutional divalent-cation impurities. Energy considerations suggest that for both AgCl and AgBr the holes are deeply trapped.

<sup>1</sup>See *The Theory of the Photographic Process*, 4th ed., edited by T. H. James (Macmillan, New York, 1977), p. 105.

<sup>2</sup>See *The Theory of the Photographic Process*, Ref. 1, pp. 145ff.

<sup>3</sup>See *The Theory of the Photographic Process*, Ref. 1, pp. 37ff.

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