

Optical and optically detected magnetic resonance studies of $\text{AgBr}:\text{I}^-$

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Low-temperature emission and optically detected magnetic resonance (ODMR) spectra of AgBr containing various amounts of iodide have been obtained. The ODMR spectrum at low iodide concentrations (1–100 ppm) is assigned to transitions of the iodine-bound exciton. Time and wavelength evolution of the emission from high-iodide-concentration (~ 3 at. %) samples provides evidence for donor-acceptor recombination. ODMR spectra of high-iodide-concentration samples suggest an iodide-related hole trap.

I. INTRODUCTION

Optically detected magnetic resonance (ODMR) is a modulation spectroscopy technique which obtains spin-resonance information on an electronically excited system through its optical emission. This technique has been used extensively to study both molecular and semiconductor crystals. Recent review articles have outlined the use of ODMR in semiconductor systems.^{1,2}

Time and wavelength evolution of the emission after pulsed excitation have been used to characterize donor-acceptor recombination in semiconductors.^{3,4} The time evolution of donor-acceptor recombination is known to follow a nonexponential decay.³ The wavelength evolution is such that the emission maximum shifts to lower energies at longer times for the recombination of neutral species (e.g., a hole trapped at an acceptor).

The emission spectra of AgBr and $\text{AgBr}_{1-x}\text{I}_x$ have been examined by various investigators.^{5–8} Nominally pure AgBr has a low-temperature emission spectrum under low-power excitation which consists of two broad bands peaking at ~ 495 nm (~ 2.50 eV) and ~ 585 nm (~ 2.11 eV).^{5,6} The 495-nm emission has been associated with an iodine-bound exciton.^{5–8} As the concentration of iodide in AgBr is increased, the 495-nm emission shifts to longer wavelengths.⁶ This emission has been associated with centers containing multiple iodide ions.⁶

The ODMR spectra of AgBr (detected at 585 nm) have been examined by several investigators.^{9,10} The spectrum of undoped AgBr consists of four resonances with g values of 1.49, 1.75, 1.81, and 2.08. The resonances at g values of 1.49 and 2.08 are assigned to free electrons and free holes, respectively, and the other two resonances are thought to be due to trapped carriers.¹⁰

The model that will be used to interpret the ODMR spectrum of $\text{AgBr}_{0.97}\text{I}_{0.03}$ is one in which “noninteracting” (exchange $\ll g\mu_B H$) electrons and holes radiatively recombine.¹ This model predicts four energy levels in a magnetic field with the electron-hole spin combinations of $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$. The $\alpha\beta$ and $\beta\alpha$ levels are radiative and thus depopulated. Resonant absorption of microwaves shifts population from the nonradiative $\alpha\alpha$ and $\beta\beta$ levels to the $\alpha\beta$ and $\beta\alpha$ levels, causing an increase in the emission intensity, i.e., a positive ODMR signal. If the electrons and/or holes are trapped at a site, their spin-

resonance characteristics (g values, hyperfine constants, etc.) are modified by the site.

II. EXPERIMENTAL

The silver bromide used in this study was prepared from 6N silver shot dissolved in distilled nitric acid. The resultant silver nitrate was precipitated by cooling the solution. The precipitate was dissolved in distilled deionized water and added dropwise to a solution of distilled hydrobromic acid. The AgBr which precipitated was washed 5–10 times with distilled water and dried in a desiccator at 40°C.

Crystals of $\text{AgBr}_{1-x}\text{I}_x$ were grown in a Bridgman furnace in a bromine atmosphere with the addition of the desired amount of AgI. Iodide levels were determined by neutron activation.¹¹ Single crystals, typically $2 \times 3 \times 3$ mm³, were cut from a boule which had been aligned by x-ray backreflection.

Samples were mounted on a rotator immersed in liquid helium at the center of a split-coil superconducting magnet. The sample was excited with the 366- or 436-nm line from a high-pressure Hg lamp. The emission was observed at right angles to the excitation with a lens-filter combination and a photomultiplier whose output was fed into a lock-in amplifier. Microwave radiation was applied to the sample from a high-power (10 W maximum) two-cavity klystron through a cut-off section of a thin-walled stainless-steel circular waveguide placed less than $\lambda/2$ from the sample. The experimental setup was calibrated by observing the diphenylpicryl hydrazyl resonance.

Two modulation variations were used. Microwave radiation could be amplitude modulated with a square wave. This produced the normal direct spectrum. The magnetic field could also be modulated with an in-line high-current transformer, amplifier, and audio oscillator. This produced the familiar derivative spectrum. For the rather broad resonances observed in AgBr and $\text{AgBr}_{1-x}\text{I}_x$, the direct spectrum was generally observed.

For the luminescence-decay experiments, the sample was excited with the 337-nm line of an N_2 laser. The laser pulses had a width [full width at half maximum (FWHM)] of ~ 0.5 ns and energies of 3–5 μJ per pulse. The emission was collected with a lens and focused through a uv-cutoff filter into a compact monochromator

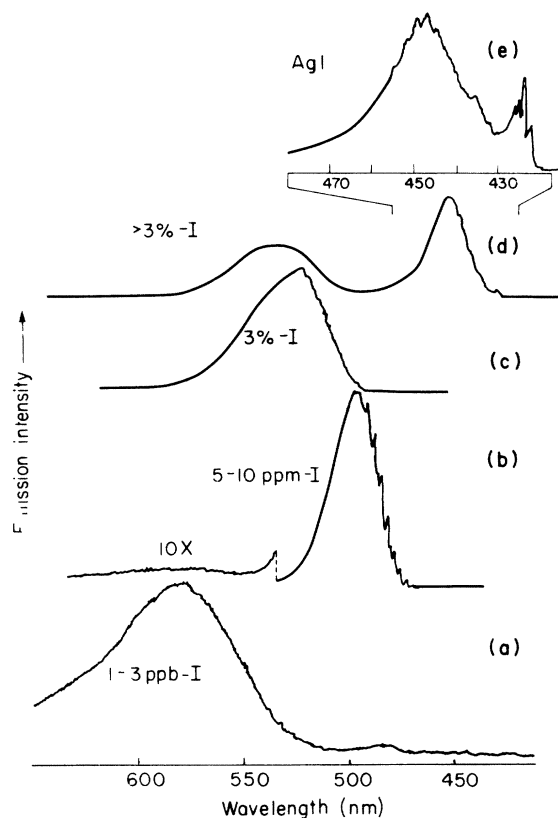


FIG. 1. (a)–(d) Emission spectra of AgBr containing various amounts of iodide (a)–(d) and (e) of AgI at 4.2 K. Samples were excited at 366 nm. The spectra are not corrected for photomultiplier response (RCA C 31034).

with a red-sensitive photomultiplier tube (RCA 4832). The spectral resolution was ~ 3 nm. Temperature variation (10–200 K) was obtained with a CTI-Cyrogenics helium refrigerator.

The photomultiplier response was fed into a Tektronix (7704A) digital processing oscilloscope. Termination in 1 k Ω gave a measured RC time constant of < 0.5 μs and was used for measurements in the range 1–200 μs . Appropriate termination resistors were used for other time ranges, and the results were merged for analysis. All emission-decay curves were the average of at least 32 transient emission signals.

III. RESULTS

Figure 1 shows the emission spectra for AgBr containing various amounts of iodide and for pure AgI, which probably contains both β and γ phases. The emission spectrum of an AgBr crystal containing very little iodide (~ 2 ppb) is dominated by the 585-nm emission band [Fig. 1(a)]. As the iodide level increases, the ratio of the intensity of the 495-nm band to the 585-nm band increases so that at above ~ 10 ppm iodide the 495-nm emission dominates [Fig. 1(b)]. At ~ 3 at.% iodide, the emission peaks at 530 nm [Fig. 1(c)]. The 585-nm emission appears to remain, but it is dominated and obscured by the much more intense 530-nm emission. At higher iodide concentrations (> 3 at.%), phase segregation appears to occur during melt crystal growth, and a new emission band appears which peaks at 452 nm (~ 2.74 eV) [Fig. 1(d)]. This new band resembles the emission of pure AgI [Fig. 1(e)]. Segregation into a AgI-like phase occurred at iodide levels of several atomic percent in the $\text{AgCl}_{1-x}\text{I}_x$ system.

Figure 2 shows the time and wavelength evolution of

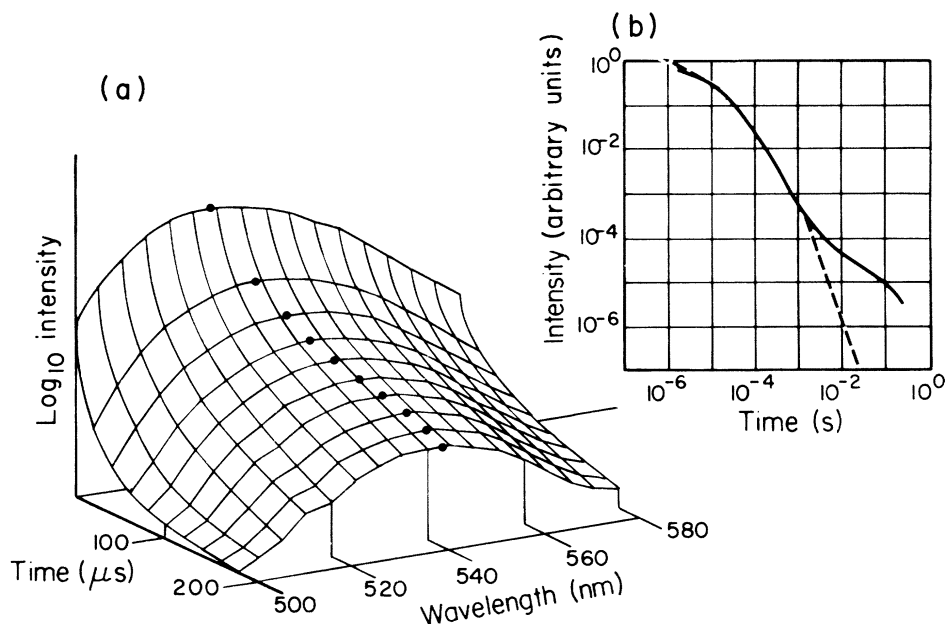


FIG. 2. (a) Logarithm of the emission intensity of $\text{AgBr}_{0.97}\text{I}_{0.03}$ at 4.2 K as a function of time and wavelength. The dots indicate the peaks of the emission spectra. (b) The log-log plot is the single-wavelength (535 nm) decay of the emission. The dashed line is a theoretical donor-acceptor decay profile for $N_D \neq N_A$, $N_A = 10^{18}$ cm^{-3} , and $W_{\text{max}} \sim 2 \times 10^6$ s^{-1} .

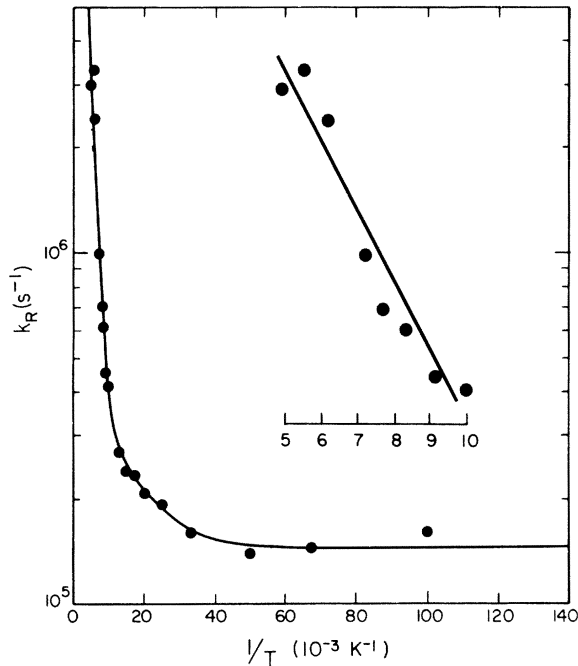


FIG. 3. Temperature dependence of the decay rate of the emission from $\text{AgBr}_{0.97}\text{I}_{0.03}$. The k_R vs $10^3/T$ plot is semilogarithmic. The higher-temperature region is shown expanded in the inset.

the 530-nm emission from $\text{AgBr}_{0.97}\text{I}_{0.03}$ at 4.2 K; Fig. 2(a) shows the emission decay as a function of wavelength at 5-nm intervals. The band maximum in this spectrum shifts to longer wavelengths as the emission decays. The band maximum is at 528 nm with zero time delay, and it is at ~ 543 nm at 200 μs after the excitation pulse. Figure 2(b) is a log-log plot of the emission decay monitored at 535 nm. The dashed line is a theoretical decay curve for donor-acceptor emission³ (*vide infra*). As the sample temperature is increased, the emission decays more rapidly and the decay becomes exponential. The temperature dependence of the decay is given in Fig. 3 as a plot of the logarithm of the recombination rate k_R versus the inverse temperature. The decay rate is taken to be the inverse of time required for the emission at 535 nm to decay to $1/e$ of its initial value. An Arrhenius fit to the higher-temperature data gives an activation energy for the quenching step, $E_a = 40 \pm 8$ meV, and a frequency factor of $(3.5 \pm 1) \times 10^7 \text{ s}^{-1}$.

The ODMR spectra at liquid-helium temperature of AgBr containing various amounts of iodide are shown in Fig. 4. The ODMR spectrum of AgBr is obtained when the 585-nm emission is monitored in samples containing modest amounts of iodide (~ 10 ppm) [Fig. 4(a)]. This ODMR spectrum decreases in intensity as the 585-nm emission becomes less intense. A different ODMR spectrum arises if the iodine-bound-exciton emission at 495 nm is monitored [Fig. 1(b)]. This spectrum consists of a broad negative peak at 4.36 kG when a microwave frequency of 35.94 GHz is used.

The ODMR spectra of $\text{AgBr}_{0.97}\text{I}_{0.03}$ [Fig. 4(c)] differ markedly from the spectra attributed to pure AgBr [Fig. 4(a)] and to the iodine-bound exciton [Fig. 4(b)]. The

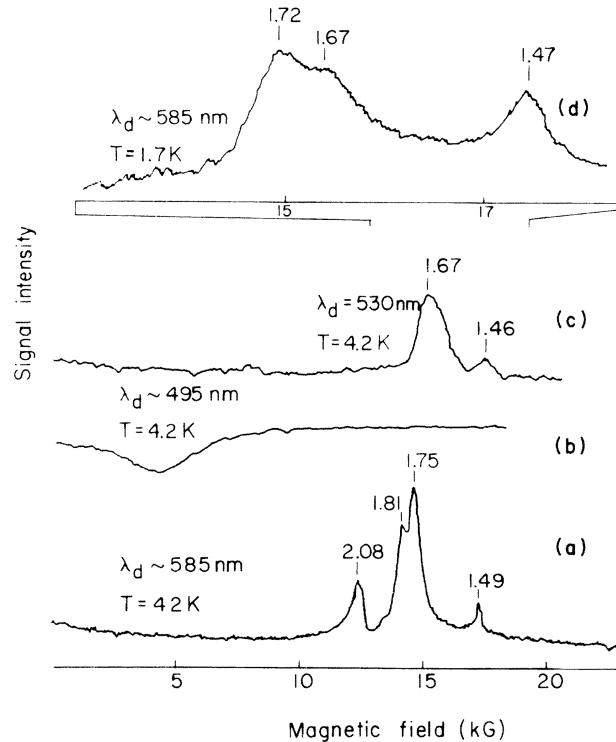


FIG. 4. (a) ODMR spectra of pure AgBr (a) and (b)–(d) $\text{AgBr}_{1-x}\text{I}_x$. Spectra were obtained by monitoring at the wavelengths (λ_d) indicated. (b) The ODMR spectrum of the iodine-bound exciton was obtained with samples containing ~ 25 and ~ 400 ppm iodide. The spectra labeled (c) and (d) were obtained on a sample containing 3 at.% iodide. g values of most resonances are given. $\nu = 34.94$ GHz.

ODMR spectrum of $\text{AgBr}_{0.97}\text{I}_{0.03}$ consists of two isotropic peaks with g values of 1.46 and 1.67. When the emission is monitored at 585 nm, an additional peak is observed with a g value of 1.72 [Fig. 4(d)]. This resonance may be the $g = 1.75$ resonance in pure AgBr.

IV. DISCUSSION

At low iodide levels an iodine-bound exciton is created by band-gap irradiation.^{5–8} This exciton is a hydrogenic species in which a hole trapped at an iodide binds an electron in a large orbit.^{5–8} The electronic structure of this exciton has been characterized as a single center with a p^5s configuration in the $j-j$ coupling limit. A more detailed characterization in terms of the solid-state symmetry has been given.⁷ The p^5s configuration gives rise to two sets of two levels. A higher-energy set with $J=0$ and 1 has not been observed. The lower-energy set of levels with $J=1$ and 2 gives rise to the 495-nm emission. The 0-0 band of this emission at 2.6409 eV is a doublet whose Zeeman spectrum confirms the $J=1, J=2$ nature of this pair.⁵ The exchange splitting of this pair is 0.1 meV (0.8 cm^{-1}) with the forbidden ($J=2$) line lying lower in energy.⁷ The ODMR spectrum shown in Fig. 4(b) arises from transitions among the angular momentum states in this exciton.

The microwave photon energy in these experiments was 0.1486 meV (1.199 cm^{-1}). An ODMR resonance [Fig.

3(b)] should occur when the magnetic field has split the $J=1$ and $J=2$ levels to a point where the difference in Zeeman energy plus the exchange splitting equals the probe energy for a pair of magnetic sublevels which differ in M_j by ± 1 . The ODMR signal is negative because population is shifted from the higher-energy emitting level ($J=1$) to the forbidden level ($J=2$) which is presumed to also have a nonradiative decay channel. This resonance was observed at 4.36 kG. Estimates from Ref. 7 suggest that it should occur at 6 ± 2 kG. These resonances might be sharper at very low iodide levels.⁷

The time evolution of AgBr_{1-x}I_x emission with intermediate levels of iodide (500–2500 ppm) has already been examined.² In this concentration range the emission behavior is intermediate to the iodine-bound-exciton and the donor-acceptor emission at high iodide levels (*vide infra*). Two peaks are observed at 2.5 and ~ 2.4 eV with different decay kinetics. The 2.5-eV peak can be identified as the iodine-bound exciton. The ~ 2.4 -eV peak was identified as excitons bound to iodide pairs.¹² The relative intensity of these two peaks was dependent upon excitation conditions.

In the high-iodide-concentration range the emission will be characterized as donor-acceptor recombination. The energy of donor-acceptor pair emission is given by

$$E_{DA} = E_g - (E_D + E_A) + \frac{e^2}{\epsilon r}, \quad (1)$$

where E_g is the energy of the band gap (2.681 eV for AgBr),⁵ E_D and E_A are the donor and acceptor binding energies, and the last term is the mutual Coulomb attraction of the donor and the acceptor,^{3,4} where ϵ is the low-frequency dielectric constant and r is the separation. This expression reduces to

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

for large values of r (long recombination lifetimes). The expression for E_{DA} in Eq. (1) assumes that the donor and the acceptor are charged in the ground state and neutral in the excited state.

The time and wavelength evolution of the 530-nm emission (Fig. 2) of AgBr_{0.97}I_{0.03} characterizes it as donor-acceptor recombination.^{3,4} The emission shifts ~ 15 nm (65 meV) to longer wavelength as it decays. This shift represents a change in donor-acceptor separation of, say, 18 to 150 Å, assuming a low-temperature dielectric constant¹³ of 10.6.

From Eq. (2) and the energy of the leading edge of the emission (~ 495 nm = 2.505 eV) at long times, the combined donor and acceptor binding energies can be estimated as follows:

$$E_D + E_A \approx 180 \pm 20 \text{ meV}. \quad (3)$$

A value of $E_A = 150$ meV has been estimated from hole-mobility studies.¹⁴ Thus, E_D is estimated to be 30 ± 25 meV. These estimates assume that E_g is not changed by the addition of 3% iodide. The most reasonable species for the shallow electron trap is an interstitial silver ion or a substitutional divalent cation. The binding energy for an electron to this species is estimated to be between 25 and 35 meV.¹⁵ The (40 ± 8) -meV activation energy determined from Fig. 3 is in reasonable agreement. At high tempera-

tures the shallowly trapped electron detraps and the distant-pair donor-acceptor recombination disappears.

The data in the log-log plot [Fig. 2(b)] are fitted with a theoretical decay curve for donor-acceptor emission.³ The parameters of this fit, $N_A = 10^{18} \text{ cm}^{-3}$ and $W_{\max} = 2 \times 10^6 \text{ s}^{-1}$, where N_A is the number of acceptor centers and W_{\max} is a transition rate, may not be exact as the emission has not yet been shown to be saturated, a necessary condition. The deviation from simple donor-acceptor behavior for times $> 10^{-3} \text{ s}$ is probably due to low-level impurities.

The ODMR spectra of crystalline AgBr_{0.97}I_{0.03} [Figs. 4(c) and 4(d)] contains a resonance at $g = 1.46$ which may be assigned to "free" electrons. The free-electron resonance has a g value of 1.49 in pure AgBr.¹⁰ The observed g shift may be due to modification of the band structure with the incorporation of iodide into the lattice. More probably the $g = 1.46$ resonance may arise from electrons which are shallowly trapped (i.e., large orbits).

The $g = 1.67$ resonance is a characteristic feature of the AgBr_{0.97}I_{0.03} system. The resonance at $g = 1.72$ seems to be the analog of the $g = 1.75$ resonance in AgBr. Thus, the $g = 1.67$ resonance can be associated with a hole trapped at a species containing "multiple iodide ions," whereas the $g = 1.72$ resonance is associated with a deeper hole trap present in pure and iodide-doped AgBr. The free-electron resonance is observed with both 530- and 585-nm detection; thus it is concluded that a shallowly trapped electron is recombining with a hole trapped in either an intrinsic center or a center containing multiple iodide ions. The suggestion that both the $g = 1.72$ and $g = 1.67$ resonances are trapped holes is supported by the absence of the free-hole resonance at $g = 2.08$.

Ideas about the center containing multiple iodide ions are speculative at this point, as no fine or hyperfine structure is observed. One possibility is a classical V_K center, composed of a hole trapped at a diatomic iodide species. Another possibility is a hole self-trapped at a silver ion with several iodide ions in the first shell (e.g., AgBr₄I₂).⁴ This would be analogous to the situation in AgCl doped with bromide ions.¹⁶ Both of these species would, however, be expected to have g values closer to 2.0 and exhibit resolved iodide hyperfine splittings.^{17,18}

An alternative description of the multiple-iodide-ion center is that it is a set of states due to an iodide-impurity band or to band tailing. These states would lie, as suggested above, ~ 150 meV above the valence band. The iodine hyperfine splittings, though large, can be accommodated in the ~ 1200 -kG linewidth of the $g = 1.67$ resonance.^{18–20} Donor-acceptor emission could occur through hole localization and electron trapping at low temperatures. Preliminary low-temperature absorption spectra on AgBr_{0.97}I_{0.03} crystals show a weak ($\alpha \sim 1$) broad absorption beyond the iodide-perturbed indirect edge.²¹ This weak absorption feature is consistent with the existence of an iodide-impurity band or band tailing.

V. CONCLUSIONS

AgBr with low amounts of iodide (1–100 ppm) exhibits an iodide-related ODMR spectrum which can be understood in terms of the model for the iodine-bound exciton. AgBr with high iodide content (~ 3 at.%) displays an

emission characteristic of donor-acceptor recombination with neutral excited states. The ODMR spectra of this system indicate that only one electron and one hole species contribute to the *iodide-associated emission*. A reasonable model for $\text{AgBr}_{0.97}\text{I}_{0.03}$ is a system with an iodide-impurity band or band-tail states ~ 150 meV above the valence band, a second "intrinsic" acceptor level somewhat further above the valence band, and shallow donor

levels, probably interstitial silver ions that trap the free electrons.

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