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Isoelectronic donor iodine and broad-band photoluminescence in TlBr

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Two different experiments on nominally undoped crystals of TlBr (indirect band gap 2.670 eV) are reported: thermal quenching of the emission bands between 2 and 100 K, and the dependence of relative intensity of emission bands on exciting intensity, at 2 K. Both support unexpectedly small binding energies, of ~ 10 meV, for electrons and holes to residual impurities. These emit broad (0.25 eV) structureless bands at 1.80, 2.20, and 2.43 eV, and are therefore expected to originate in tightly bound centers. Their origin is known only for the 2.20-eV band, which is due to the recombination of an exciton bound to the isoelectronic impurity iodine. Thermal quenching of the emission bands shows two activation energies for the 2.20-eV band. These are identified with a binding energy of 37 meV for the hole to the iodine, and 2 meV for that of the electron to the system (iodine-hole). For the 2.43-eV band a single activation energy of 4 meV is identified with the binding energy of an exciton to an unknown defect. Other isoelectronic systems are compared with TlBr:I. Their possible connection with induced infrared absorption is suggested. Finally, the direct edge emission found in TlBr in the vicinity of 3.000 eV is discussed, and found to be anomalous in view of recent results showing its band gap to be indirect.

INTRODUCTION

TlBr is a photoconducting phosphor (semiconductor) with an indirect gap (X_6^+-R_6^-) of 2.670 eV (4 °K) (Ref. 1) and a direct gap (X_6^+-X_6^-) of 3.016 eV (4 °K).[2] The X_6^+-R_6^- gap is unusual[1] in that a transition from the highest maximum of the valence band at X_6^+ to the lowest minimum of the conduction band at R_6^- is indirect *forbidden* in contrast with Ge, Si, GaP, and the silver halides which are indirect *allowed*. The binding energy of the exciton to the X_6^+-R_6^- and X_6^+-X_6^- gap is 23 meV,[1] and 9.8 meV,[3] respectively. Sharp-line fluorescence near the X_6^+-X_6^- gap has been reported and attributed to the decay of excitons, free and bound to impurities.[4,5] Similar data for the X_6^+-R_6^- exciton have also been reported.[5] Recently, Nakahara and Kobayashi,[6] using extremely pure samples, find that the X_6^+-R_6^- edge emission consists entirely of the decay of free excitons with cooperation of phonons necessary for the conservation of crystal momentum and the decay of the exciton molecule. Excitons bound to impurities are not observed in these extremely pure samples. These authors also observe that impurity excitons can be observed, but at the expense of completely quenching the X_6^+-R_6^- intrinsic exciton emission. They find that the addition of iodine, a likely impurity, of amount 10^{-6}–10^{-5} mole fraction completely quenches the intrinsic X_6^+-R_6^- exciton emission, replacing it with a broad emission band at 2.20 eV. Since the 2.20-eV emission band increases linearly with iodine concentration they conclude that it is due to the decay of an exciton localized at the iodine impurity.

In our work with nominally undoped commercially available crystals at 4 °K, we have never observed intrinsic X_6^+-R_6^- exciton emission but only several broad (0.25-eV) emission bands. These are the subject of this paper. The most prominent of these bands is the iodine band at 2.20 eV. This agrees with the observations of Nakahara and Kobayashi[6] if we assume that even though our crystals are nominally undoped they contain a sufficient concentration of iodine and other impurities to quench the intrinsic X_6^+-R_6^- exciton emission.

The iodine emission band at 2.20 eV is of particular interest since iodine is isoelectronic to bromine.[7,8] This work reports results on the thermal quenching of these emission bands and was motivated by the preliminary observation of unexpectedly large thermal quenching between 4 °K and 77 °K, and a dependence on exciting intensity of their relative intensities at 2 °K. Both observations are unexpected because the peak intensities of the emission bands lie well within the X_6^+-R_6^- band gap and therefore are expected to be due to recombination at "deep" impurities which should be insensitive to change of temperature, or exciting intensity at low temperature. Our results show that the emission bands studied are, in fact, due to "shallow" impurities of binding energy of ~10 meV in spite of the fact that they are structureless and broad (0.25 eV), and located well within the X_6^+-R_6^- band gap. These results on impurity emission in TlBr appear contrary to common notion and experience according to which broad structureless emission bands well within the band gap are due to deep, well localized impurities.

RESULTS AND DISCUSSION

Data were obtained on three nominally undoped commercially available crystals of TlBr purchased at widely different times from the same source. Since their characteristics differ in detail we assume that they came from separate boules, each grown at a different time. Impurity gradients exist as shown by small changes in the relative intensity of the emission bands when the exciting light was focussed on different parts of the crystal. The temperature was changed by adjusting the flow of cold helium gas over the sample. Temperature was measured by a silicon diode embedded in a copper block to which the sample was attached. After cutting, the samples were polished and etched with water. The thermal quenching of the emission bands is essentially the same in all three samples. The data to be presented may therefore be considered as typical for TlBr containing the impurities of our samples. The defects responsible for the emission bands are known only for the 2.20-eV band. It is the isoelectronic impurity iodine.[6]

A. Thermal quenching of emission bands

Figure 1 shows the emission spectrum, at different temperatures, for constant intensity of the exciting light. At low temperature it is in substantial agreement with the work of Marquardt and Williams[9] performed at 10 °K. Figure 2 plots the logarithm of the integrated intensity of each band versus $1/T$ and lists the appropriate activation energies. These are, indeed, unexpectedly small considering the half-width of the bands (~0.25 eV) and their peak energies with respect to the X_6^+-R_6^- energy gap $E_g = 2.670$ (4 °K), both indicating tightly bound centers. Figure 1 also shows an increase of the peak energies with temperature of ~20 meV (2–40 °K), particularly evident in the 2.20-eV band. We note that the energy of the $n=1$ X_6^+-R_6^- forbidden exciton shifts upward by 17 meV (2–20 °K).[1] This is larger than the case for the X_6^+-X_6^- allowed exciton, ~10 meV (2–40 °K).[2,3] The 2.43-eV band has a single activation energy of 4 meV (20–30 °K), the 2.20-eV iodine band two activation energies of 2 meV (8–16 °K), and 37 meV (60–100 °K), separated by an exhaustion region (20–60 °K).

Discussion will be focused on the 2.20-eV emission band due to the iodine. We shall equate experimentally determined activation energies with binding energies, assuming this identification is correct. At low temperature the cause of the emission has been conjectured[6] to be the radiative decay of the X_6^+-R_6^- exciton localized at the iodine. The process leading to the initial state "iodine-exciton" may either be the capture of a free exciton, or the sequential capture of electron and hole. Their relative probabilities are unknown. Because the relative electronegativity of bromine with respect to iodine is +0.53,[10] the system (iodine-electron) is expected to be unstable.[8] If so, the hole will be captured first, and then the electron. We shall assume this to be the case. When the sample is warmed the number of activation energies observed depends on the magnitude of the individual binding energies: free excition E_{ex}, hole to iodine E_h, and electron to the system (iodine-hole) E_e. Clearly, the system (iodine-exciton) will exist only if $E_e + E_h > E_{ex}$. If $(E_e + E_h) - E_{ex} < E_{ex} < E_e$, or

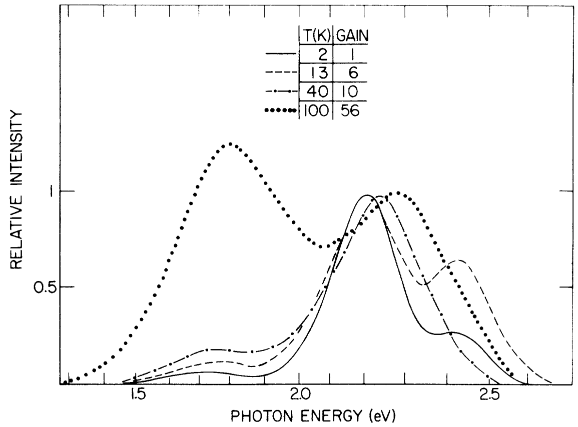

FIG. 1. Broad-band photoluminescence spectrum of nominally undoped crystal of TlBr as a function of T (°K). Spectra are uncorrected and normalized to intensity of 2.20-eV band at gain shown. Exciting radiation 3650 Å. Detector: cooled RCA 7102 photomultiplier.

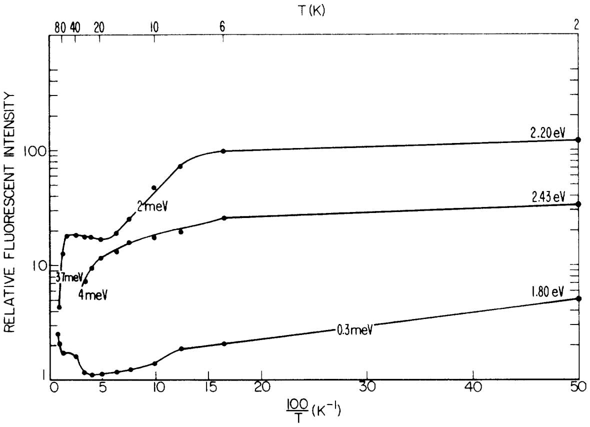

FIG. 2. Plot of $\log_{10}$ (integrated intensity) vs $1/T$ of 1.80-, 2.20-, and 2.43-eV bands of crystal the spectrum of which is shown in Fig. 1. Activation energy E, defined as slope of $\ln I$ vs $(kT)^{-1}$, is appropriately shown in the figure. At higher T the increase of intensity of 1.80-eV band which occurs simultaneously with quenching of 2.43 eV and the 2.20 eV is due to operation of Schön-Klasens mechanism for energy transfer discussed in text.

if $(E_e + E_h) - E_{\mathrm{ex}} > E_{\mathrm{ex}} < E_e$, a single activation energy will be observed. This activation energy, in the first case, is the binding energy of the system (iodine-exciton); in the second case, it is that of the system (iodine-electron-hole). If $(E_e + E_h) - E_{\mathrm{ex}} > E_e < E_{\mathrm{ex}}$, a single activation energy E_e will be observed if $E_e \geq E_h$, but if $E_e \ll E_h$, there will be *two* activation energies, E_e and E_h, as in Fig. 2 for the 2.20-eV band. We, therefore, conclude that $E_h = 37$ meV, and $E_e = 2$ meV, are the binding energy of the system (iodine-hole), and the electron to the system (iodine-hole), respectively. We further conclude that in the range 2–6 °K recombination is bound-bound and that in the range 20–100 °K the thermalized electron recombines with the trapped hole (free-bound). In order that thermal quenching be observable we must assume that the bound-bound transition probability exceed that for free-bound transitions, or that a nonradiative recombination path open to the free electron is closed to the bound electron. Conceivably, both quenching mechanisms are effective, the data are noncommittal on this point.

The 2.43-eV band shows a single activation energy of 4 meV. If it is due to an exciton trapped at an unknown impurity then it must be the binding energy of exciton to impurity since $E_{\mathrm{ex}} = 23$ meV.[1] Alternatively, this band may be due to free-bound recombination of a free electron (hole) with a bound hole (electron).

B. Dependence of relative intensity of emission bands on exciting intensity

We shall now show that the binding energy of 2 meV for the electron to the system (iodine-hole), found by the technique of thermal quenching, is supported by a different experiment. Figure 3 shows that at 2 °K, a dependence on exciting intensity *J* of the relative intensity *I* of the individual emission bands. To be brief, we shall refer to this dependence as a *J-I* shift. The excitation spectra of these emission bands are shown in Fig. 4 which also includes the absorption and photoconductivity spectra. The coincidence of the thresholds of the different spectra shows that TlBr is a photoconducting phosphor.

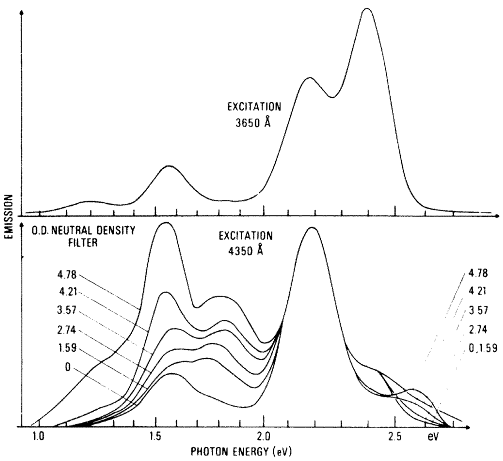

FIG. 3. Below: Dependence on exciting intensity of emission bands of nominally undoped crystal of TlBr at 2 °K. Exciting light 4350-Å line of high pressure Hg arc varied from full intensity with neutral density filters of indicated optical density. The exponent of $I = J^n$ dependence of 2.20-eV band is 1.06. Crystal used is from a different boule than that used in Fig. 1 and shows an additional band at 1.55 eV. At higher temperature the 1.55-eV band dominates and quenches ~200 °C, but irreversibly unlike bands shown in Fig. 1. Above: Emission spectrum excited with undiminished intensity of 3650-Å Hg line, ~0.1 emission compared with 4350 Å excitation. Detector: cooled RCA 7102 photomultiplier.

If, as indicated by the thermal quenching data, the binding energy of the impurity species are small, then a *J-I* shift at 2 °K can be rationalized by the Schön-Klasens[11] mechanism for the transfer of energy between them. This mechanism was originally proposed to explain the transfer of energy between two acceptor species by the transfer of holes via the valence band. We shall review it briefly using this concrete example although the two species could be two donors, or two bound excitons, for example, communicating via the conduction, or free-exciton band, respectively. The essential point is that energy between the two species be transferred by the movement of charge between them via a band. In the example chosen, each acceptor species binds a hole which is as-

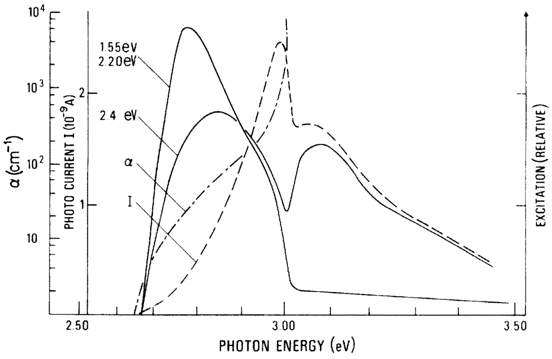

FIG. 4 Uncorrected excitation spectra, at 2 °K, of emission at 1.55, 2.20, and 2.43 eV. The gain *G* at various energies is $G(2.43\ \mathrm{eV}) = G(1.55\ \mathrm{eV}) = 5G(2.20\ \mathrm{eV})$. Source 450-W xenon arc. The spectra of $\alpha(20\ °\mathrm{K})$ and uncorrected photocurrent (2 °K) are also shown. Detector: cooled RCA 7102 photomultiplier. Sample: same as in Fig. 3.

sumed to combine radiatively with a free electron (free-bound transition). When $T>0$, the acceptors are coupled through a heat reservoir at T. Then the significant thermal process is the thermal emission of a hole from the shallower acceptor into the valence band, a monomolecular reaction the rate of which is fixed by the temperature. It will compete with the recombination of an electron in an acceptor and a hole in the valence band, a bimolecular reaction the rate of which depends on the exciting intensity J. When thermal release and recombination are competitive a decrease of J (or an increase of T) will release holes from the shallower acceptor into the valence band whence they are captured by the deeper acceptor, leading to a shift of hole concentration, and therefore to a J-I shift. Assuming a band density of states of ~10^{19}, we estimate a species must be bound by ~1 meV if it is to transfer energy to another more tightly bound species at 2 °K. The binding energy of the electron to the system (iodine + hole), found to be 2 meV by thermal quenching, is thus seen to be consistent with the J-I shift shown in Fig. 3 demonstrating a transfer from the 2.20-eV band to other bands.

We would like to add that in order to observe a J-I shift it is important to bring the recombination rate, which is determined by J, into competiton with thermal release, which is fixed by T. As an example, Gisolf and Kröger[12] find that a ZnS-MnS phosphor emitting blue and yellow emission bands shows a J-I shift at 300 °K but not at 77 °K. In the case of TlBr at 2 °K we find a J-I shift when exciting with 4350 Å but not 3650 Å. The reason for this is the large difference of J for the two exciting wavelengths. J(photons absorbed cm^{-3} sec^{-1}) $= \alpha E^{-\alpha x}$ where α (cm^{-1}) is the absorption coefficient, E(photons cm^{-2} sec^{-1}) is the irradiance; α(3650 Å)/α(4350 Å) $= 10^6$. To bring the recombination rate into competition with thermal release Gisolf and Kröger changed T; we changed the initial value of J. Instead of changing J at a fixed wavelength with neutral density filters, as was done for the results shown in Fig. 3, J can also be changed by shifting the exciting wavelength to lower absorption coefficients. We find a J-I shift for either way of changing J.

A comparison of this work with previous work on isoelectronic traps is shown in Table I. The case of AgBr:I is interesting. The emission spectrum of AgBr:I exhibits a weak no-phonon line at 2.6412 eV (4 °K) followed by stronger phonon-coupled emission lines.[13] The latter broaden, increase in strength, and finally merge into a continuum constituting a vibronic band peaking at 2.50 eV. This band has been studied by Mozer and Lyu[14] and also occurs in nominally undoped AgBr due to iodine as an impurity.[14] The thermal quenching of the 2.50-eV band in AgBr also shows a high- and low-temperature region of quenching separated by an exhaustion region.[15] However, unlike its analog in AgBr:I, the 2.20-eV band of TlBr:I is not preceded by line structure due to a no-phonon transition and its cooperation with phonons. The absence of such structure points to strong phonon cooperation; the 2.20-eV band is thus due to the domination of vibronics in the transition. In this respect it resembles the 2.07-eV emission band of CdS:Te.[16] In fact, except for CdS:Te and TlBr:I the emission of all the isoelectronic impurities listed in Table I show no-phonon transitions. This might be expected for CdS:Te for which the hole binding energy is[16] ~190 meV but not for TlBr:I for which we find a hole binding energy of only 37 meV. From the binding energy of the electron and hole to the iodine and the X_6^+-R_6^- band gap of TlBr we calculate that the no-phonon line should appear at 2.631. Thus, the energy separation (zero-phonon line to vibronic band peak) is 0.43 eV. For AgBr:I and CdS:Te the same quantity is 0.14 and ~0.29 eV, respectively.

In AgBr, Brandt and Brown[17] have shown that by illuminating AgBr crystals at 9 °K with band-band light, absorption in the infrared can be induced (induced-infrared absorption). We suggest that this effect may be due to the absorption of infrared photons by a loosely bound electron moving adiabatically in the field of a more tightly bound hole, both attached to the iodine in AgBr:I. This suggestion does not contradict the conclusion of Brandt *et al.*[18] establishing the no-phonon induced infrared transition as a transition from a $1S$ to a $2P$ state by a study of its Zeeman effect. The induced-infrared absorption would thus be analogous to the infrared spectra arising from foreign atoms in elemental semiconductors.[19] In the former case it is necessary to pump the crystal with band-gap light to populate the infrared absorbing center, possibly iodine in the case of AgBr.

Finally, we would like to comment on the interesting fact that TlBr shows edge emission from both the indirect X_6^+-R_6^-,[6] and the direct X_6^+-X_6^- gap.[4,5] Of all indirect-gap materials, it is unique in this respect. The X_6^+-X_6^- (Ref. 4) emission consists of several lines, one of which is resonant with the X_6^+-X_6^- free-exciton absorption studied by Bachrach and Brown.[2] This emission line was therefore assigned to the radiative decay of the free X_6^+-X_6^- exciton, the others to X_6^+-X_6^- excitons bound to impurities.[4] Since the X_6^+-X_6^- exciton is observed in emission it was concluded that the gap must be direct rather than indirect. It was argued[4] that were the gap indirect rather than direct, then the X_6^+-X_6^- exciton emission would be negligible

TABLE I. Isoelectronic traps and relevant data. Binding energy of bound exciton is referred to band gap. Column labeled "Trap" designates particle captured first (electron or hole), and its binding energy. This table is a correction and extension of Table I of Ref. 8, to include results of this work. In column 2 dir. is direct and indir. is indirect.

Host lattice:impurity	Energy gap (eV)	Bound exciton (meV)	Free exciton (meV)	Trap Type	Trap (meV)
CdS:Te	2.582[a] dir.	~250[b]	29[a]	*h*	~190[c]
ZnTe:O	2.393[d] dir.	404[e]	12[d]	*e*	400[e]
GaP:Bi	2.339[f] indir.	107[e]	10[f]	*h*	50[e]
GaP:N	2.339 indir.	21[e]	10	*e*	8[e]
AgCl:I	3.254[g] indir.	46[g]		*h*	
AgBr:I	2.711[h] indir.	43[g]	16[h]	*h*	
TlBr:I	2.670[i] indir.	39[j]	23[i]	*h*	37[j]

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[c] Reference 16.

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[f] P. J. Dean and D. G. Thomas, Phys. Rev. 150, 690 (1966).

[g] Reference 13. For the binding energy of bound exciton in AgCl:I a lower and upper limit of 34 and 46 meV, respectively, is given. We list the latter. If 34 meV is chosen, the energy gap becomes 3.242 eV.

[h] G. Ascarelli, Phys. Rev. Lett. 20, 44 (1968).

[i] Reference 1.

[j] This work.

because of an extremely unfavorable occupation probability due to the Boltzmann factor, in spite of the fact that the X_6^+-X_6^- transition probability may exceed that of X_6^+-R_6^- by many orders of magnitude. This was demonstrated for Ge by Haynes and Nilsson.[20] Nevertheless, Nakahara *et al.*[1] have demonstrated that the gap of TlBr is, in fact, an indirect X_6^+-R_6^- gap. They[21] also observe that Hg-arc excitation, used in Refs. 4 and 5 to excite the X_6^+-X_6^- emission, does not excite this emission in their pure samples but that a pulsed N_2-laser excitation does. Since a major impurity of the "nominally pure" samples used in Refs. 4 and 5 probably is iodine, and these workers used extremely pure samples, it seems that the X_6^+-X_6^- edge emission may be connected with the presence of iodine. However, we are unable to suggest an explanation for the connection between small concentrations of the iodine impurity and the X_6^+-X_6^- edge emission.

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