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Exciton Emission and Donor-Acceptor Association in Thallium Bromide

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Free- and bound-exciton emission with longitudinal optical (LO) phonon cooperation is reported in undoped TlBr. The binding energies of the bound excitons with respect to the free exciton are 4 and 7 meV, respectively. A photocurrent peak at the energy of the free exciton at 4 K is interpreted as due to an Auger process at the bound-exciton complexes. Extrinsic photocurrent is reported. The temperature dependence of its excitation spectrum is anomalous from the point of view of the conventional Riehl-Schön recombination model and is shown to be consistent with a model involving donor-acceptor pairs.

INTRODUCTION

Strong exciton absorption in TlBr in the region of the fundamental edge was first observed by Pleil,¹ although it was not initially recognized as such. Nikitine and Reiss² first attributed this absorption to an exciton. This was confirmed by Tutihasi,³ Lefkowitz *et al.*,⁴ and more recently by the extensive work of Bachrach and Brown⁵ on strain-free films. The latter, in addition, interpret a peak at slightly larger energy than the exciton peak, and separated from it by somewhat less than the energy of a longitudinal optical (LO) phonon, as an exciton-phonon bound state. This is a new quasiparticle proposed by Toyozawa and Hermanson⁶ to explain an anomaly in phonon cooperation in exciton emission and absorption, respectively. The anomaly consists of the observation that, in some materials, the position of the lines due to cooperating phonons is not symmetrical with respect to the no-phonon exciton line. In particular, in optical absorption, the separation of the exciton peak from a higher energy companion is less than the energy of the LO phonon. In emission, on the other hand, this separation is equal to the LO phonon. The idea of the exciton-phonon bound state has recently been elaborated on by Toyozawa⁷ and Sak.⁸ In addition, Bachrach and Brown⁵ determined the exciton effective mass from the Faraday-rotation pattern of the exciton line and the binding energy of the exciton (6.5 meV) from the oscillatory magnetoabsorption.

In this paper we shall demonstrate radiative recombination via free and bound excitons as well as an Auger process, a competing radiationless process, for bound excitons in which the bound-exciton energy appears as kinetic energy of one of the particles by ejection into its respective conduction band. Finally, nominally pure TlBr, just as TlCl,⁹⁻¹¹ will be shown to exhibit marked extrinsic photoconductivity. The spectrum of extrinsic photocurrent will be shown to exhibit an anomalous temperature dependence and suggest donor-acceptor pairing instead of isolated defects.

CRYSTALS AND EXPERIMENTAL TECHNIQUES

TlBr is cubic and has CsCl structure. It is distinguished by an unusually large static dielectric constant¹² 30.4 (290 K), which increases to 35.1 (1.5 K). Its band gap at 4 K is 3.016 eV and the binding energy of the free exciton is 6.5 meV.⁵ The change of band gap with temperature is anomalous, increasing as the temperature increases. This was noticed early by Fesefeldt¹³ and confirmed by other workers⁵ and is a property shared by TlCl.¹⁴ Some of the physical properties of TlBr have been tabulated in Ref. 5.

The nominally undoped single crystals of TlBr used in this work were obtained from two commercial sources. After cutting and polishing, the samples were annealed for 12 h at 250 °C as suggested by Smakula.¹⁵ Without annealing, the linewidths of the exciton emission to be reported below were much wider. The electrodes used in the

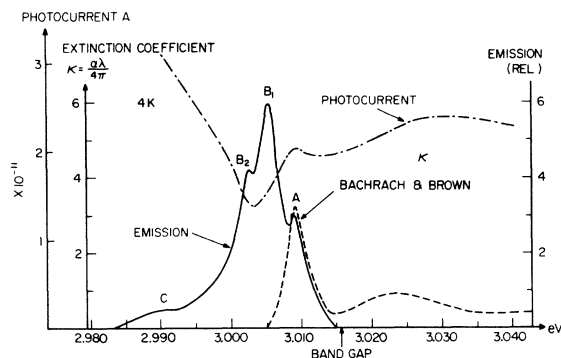


FIG. 1. Exciton emission and excitation of photocurrent 4 K. Optical absorption from Bachrach and Brown [Phys. Rev. Letters **21**, 685 (1968)]. In order to observe the exciton contribution to the photocurrent, the extrinsic component, shown in Fig. 2, must be suppressed. Full scale, 3×10^{-11} Å; suppression 4×10^{-8} Å. Free exciton A, bound excitons B_1 and B_2 , LO phonon C.

photoconductivity measurements were silver paint. For the emission spectra, the exciting source was a 200-W high-pressure Hg arc lamp focused by quartz lenses on the sample to give an $f/0.5$ illumination aperture. The exciting radiation was filtered by a line filter at 4050 Å of 34-Å bandpass for the measurement of the exciton emission because experience showed that exciting in this manner gave the strongest exciton emission. The emission, gathered from the excited surface, was focused on the slit of a monochromator ($f/7$) using a 1200-lines/mm grating blazed at 7500 Å in second order and detected photoelectrically using a preamplifier and phase-sensitive detector. Photocurrents were measured dc by a picoammeter and excited by a 450-W xenon arc lamp through a double monochromator with quartz prisms for extrinsic photocurrents. In the exciton region the grating instrument described above was used.

RESULTS AND DISCUSSION

A. Edge Emission and Photoconductivity

Figure 1 shows the edge emission at 4 K on which is superimposed the absorption spectrum found by Bachrach and Brown.⁵ The spectrum shown is typical of a number of samples. In some, the relative intensity of the peaks differed from that shown; in others, the peaks were not as well resolved; and finally, in some samples, the peaks were not resolved at all. In order to get a "good" spectrum, it is necessary that the samples be properly annealed. However, this seems not to be sufficient. Some properly annealed samples showed a spectrum in which the peaks shown in Fig. 1 are poorly resolved or not resolved at all, peaks A, B_1 ,

and B_2 being encompassed by a single broad peak. Care must be exercised in mounting the samples as strain free as possible because they are "soft" and plastically deform easily.

It is suggested that peaks B_1 and B_2 result from the radiative recombination of excitons bound to unknown defects. The binding energies with respect to the free exciton are 4 and 7 meV, respectively. The interpretation given seems reasonable in view of similar observation¹⁶ on bound excitons in group II-VI compounds, CdS for example. Peak A is assigned to the resonance emission due to the radiative annihilation of the $n=1$ intrinsic exciton. It is seen from Fig. 1 that the intensity of A is comparable with that of the defect bound excitons B_1 and B_2 . This contrasts with similar observations on the II-VI compounds or copper halides¹⁷ in which the intrinsic exciton emission is typically small compared with that of the bound excitons. For TlBr this indicates a relatively smaller capture cross section of defects for free excitons which may be caused by the large dielectric constant.

In addition to the free and bound excitons A, B_1 , and B_2 , a weak relatively broad band marked C is shown in Fig. 1. The energy of C referred to as the "center of gravity" of A, B_1 , and B_2 is 14 meV. We assign C to the photon emitted when the exciton, free or bound, returns to its ground state with the cooperation of an LO phonon at $q=0$. The basis for this assignment is the work of Cowley and Okazaki,¹⁸ who determined the phonon dispersion curves of TlBr by inelastic neutron scattering. From their data the energy of the single LO mode at $q=0$ is 14.3 meV. The fact that only the LO mode is observed seems reasonable since, in the first place, the longitudinal phonon exciton interaction is expected to be large compared to that of transverse phonons.¹⁹ Second,²⁰ for exciton radii (54 Å for TlBr)⁵ large compared to the lattice constant (3.97 Å for TlBr), both the LO and longitudinal acoustic (LA) phonon exciton interactions are expected to be weak. Moreover, when the radius of the exciton to the lattice constant is large, the interaction of the exciton with the LO phonon is expected to be much stronger than with the LA phonon.²⁰ A comparison with CdS is of interest in this connection. Hexagonal CdS has lattice constants 4.13 and 6.75 Å and the radius of the $n=1$ exciton is 28 Å.²¹ Indeed, in CdS the emission of bound excitons with phonon cooperation is weak and is principally via LO phonons.²²

Figure 1 also shows the spectrum of photocurrent at 4 K. The coincidence of the photocurrent peak with the exciton absorption line suggests the participation of excitons in photoconductivity. The spectrum of photocurrent shown in Fig. 1 is obtained only when the extrinsic photocurrent, to be discussed below, is suppressed. Clearly, thermal

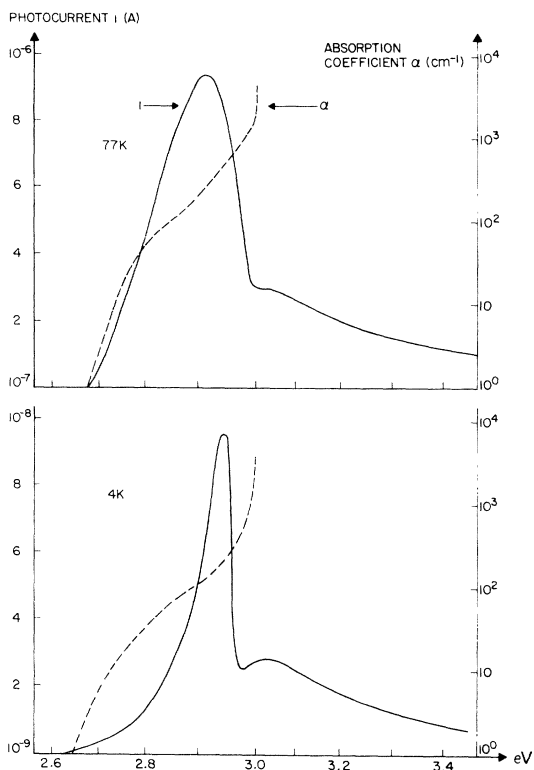


FIG. 2. Excitation of photocurrent at 4 and 77 K uncorrected for xenon arc lamp. Applied voltage 100 V. Absorption coefficient from Pleil (Ref. 1).

dissociation of the exciton at 4 K is not probable. We propose that the production of free carriers at the energy of the free exciton takes place through an Auger process²³ at defects to which the free excitons are bound. In the Auger process it is necessary that the exciton be bound to conserve momentum. The energy of the bound-exciton complex is converted into kinetic energy of one of its particles (electron or hole) by ejection high into its respective conduction band.

As to connection with previous work, that of Bachrach and Brown⁵ seems most appropriate. These authors have called attention to the importance of strain-free samples in their investigation of the optical properties of TlBr. Indeed, the spectrum shown in Fig. 1 was obtained only with carefully annealed samples. Moreover, in absorption, these authors do not find cooperation with the free LO phonon but attribute the hump on the high-energy side of the exciton absorption shown in Fig. 1 to an exciton-phonon state in which the two quasiparticles, exciton and phonon, are bound. This is the exciton-phonon bound state,⁶ or more exactly, an exciton-phonon quasibound state⁷ since the phonon energy (14.3 meV) is larger than the binding energy of the

exciton (6.3 meV). The exciton-phonon bound state would not be seen in emission since apparently the lifetime of the quasiparticle against decay into a free phonon and exciton is short.⁸ In exciton emission with phonon cooperation we are thus dealing with a different situation: A free exciton or one bound to a defect decays with the emission of a photon and a *free* phonon. Further connection with the work of Bachrach and Brown is provided by their determination of the free-exciton binding energy of 6.5 meV. At 77 K ($kT = 6.5$ meV) we are unable to detect exciton emission which, in view of the binding energy, seems reasonable. Finally, we note that by analogy with CdS²⁴ the bound-exciton lines in TlBr are rather broad, about 3 meV, the same as the free-exciton line. In CdS the free-exciton lines are 3 meV wide, while the bound-exciton lines, on the other hand, are 0.3 meV wide. This may be due to strain broadening introduced in the cooling of the sample.

B. Extrinsic Photoconductivity

Figure 2 shows the spectral response of the extrinsic photocurrent at 4 and 77 K. Part of the extrinsic response at 4 K is also shown in Fig. 1. The optical absorption coefficient, replotted from the data of Pleil,¹ is superimposed. All TlBr investigated by us shows extrinsic photoconductivity. This is also true of TlCl as shown by other workers.⁹⁻¹¹ It might be thought that these results are intrinsic rather than extrinsic, specifically, that the optical absorption and photocurrent shown in Fig. 2 are due to an indirect gap at 2.6 eV. This idea, however, is untenable with the existence of exciton emission (3 eV) at 4 K. Exciton emission from the direct gap would be negligible because of an extremely unfavorable occupation probability due to the Boltzmann factor, in spite of the fact that the transition probability from the direct gap may exceed that from the indirect gap by many orders of magnitude.²⁵

We call attention to the shape of the spectral response of the extrinsic photocurrent at 4 K and the difference between it and the corresponding curve at 77 K. The rest of this paper will be devoted to arguing that these results are not in agreement with the conventional Riehl-Schön²⁶ (RS) model for recombination in a semiconductor (photoconducting phosphor) and that the data of Fig. 2 are in better agreement with the donor-acceptor pair model of Prener and Williams²⁷ (PW).

The RS model provides only for transitions between two states that are free or between a state that is bound and one that is free. The excitation of extrinsic photocurrent, for example, is a transition between an empty acceptor (initial state) and a final state consisting of an electron in the conduction band and a hole on the acceptor. At temperatures at which the cooperation of phonons by phonon

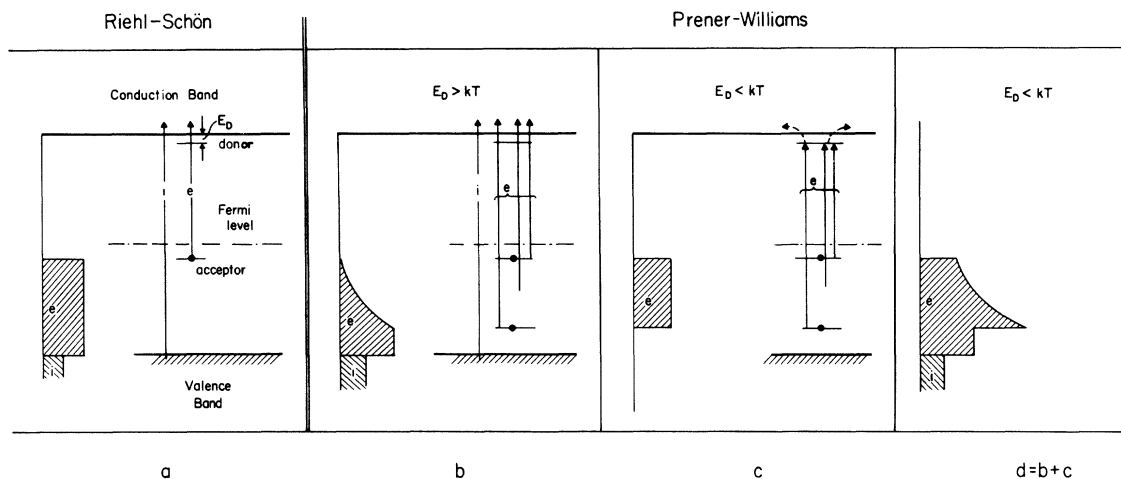


FIG. 3. Schematic representation of RS vs PW model of a semiconductor (photoconducting phosphor). In the RS model donors and acceptors are independent, in the PW model, associated. In the latter, association is indicated by drawing several ground states for a single acceptor. This is forced by the attempt to represent pair levels in a diagram valid only for single-particle states. The acceptor is assumed "deep" and the *excited* shallow donor state, shown in the figure, is thermally ionized if $E_D < kT$. (a) In the RS model the photocurrent is due to the photoionization of the electron of an empty acceptor. Its spectrum is approximately independent of T and has a *single* threshold [Eq. (1)]. (b) In the PW model, when $E_D > kT$, the photocurrent is due to the photoionization of pairs which, in this model, have *different* thresholds [Eq. (3)]. (c) When $E_D < kT$ the photocurrent due to thermal ionization of the shallow excited donor of the photoexcited pair [Eq. (2)] must be added to the component shown in (b) to give the total excitation (d).

absorption is negligible, the spectrum of the excitation of extrinsic photocurrent is expected to be independent of temperature. We shall discuss its shape at low temperatures below when we compare the RS model with the PW model.

The frame of the PW model is wider than that of the RS model because, in addition to the transitions of the RS model, transitions between bound states are also permitted in the form of donor-acceptor pair transitions. The transition energies involving a bound state are

$$h\nu = E_g - E_A \quad (\text{RS}), \quad (1)$$

$$h\nu(r) = E_g - (E_A + E_D) + e^2/Kr \quad (\text{PW}), \quad (2)$$

$$h\nu(r) = E_g - E_A + e^2/Kr \quad (\text{PW}). \quad (3)$$

The initial states in (1), (2), and (3) are an empty acceptor and pair, respectively. E_g is the energy gap, E_A and E_D the depths of isolated donor and acceptor, r is their separation. Equation (2) is the standard equation for the transition energy from the ground state (empty pair) to the final state in which an electron and a hole are excited in the pair. It is asymptotically correct for large r . Equation (3) is the transition energy from the pair ground state to the final state consisting of an electron in the conduction band and a hole in the pair. It follows from Eq. (2) by noting that in first order the binding energy of the electron is unaffected by the *neutral* acceptor and is given to good approximation by E_D . Equation (1) describes the same situation

for the RS model in which, of course, we are dealing with an isolated acceptor. In Eqs. (1) and (3) $h\nu$ represents a *threshold* energy. Note that in the RS model the threshold energy is independent of r , but not in the PW model. This fact results in different spectral shapes for the excitation of extrinsic photocurrent in the two models. This is sketched in Fig. 3(a)(RS) and Fig. 3(b)(PW), respectively, for conditions in which the contribution to the extrinsic photocurrent of states created by the process described by Eq. (2) is negligible. This will be the case if thermal dissociation and Auger processes involving these states are negligible. We thus conclude from the shape of the spectrum of extrinsic photocurrent at 4 K that the appropriate recombination model is very likely that of PW.

This conclusion is supported by the change of the excitation spectrum of extrinsic photocurrent in going from 4 to 77 K. From the point of view of the RS model, the spectrum should be approximately independent of temperature, in contradiction to our results. The PW model, on the other hand, provides for such a change by the thermal ionization of donor electrons from excited pairs created by the process described by Eq. (2). In fact, shallow excited donor states of the pair have a higher probability of excitation than deeper donor states because of the overlap they provide with the acceptor wave function. The contribution to the extrinsic photocurrent of thermally ionized shallow donor electrons of excited pairs is sketched in Fig.

3(c). In this regime the extrinsic photocurrent is the sum of that shown in Figs. 3(b) and 3(c) and is shown in Fig. 3(d).

Summarizing, we conclude that the shape of the spectrum of extrinsic photocurrent at 4 K and the change of this spectrum in going to 77 K support the donor-acceptor pair recombination model of PW

rather than that of RS.

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“Off-Center” Effect in the Relaxed Excited State of Cu⁺ Substitutional in Alkali Halides

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Lifetime data on the $3d^9 4s \rightarrow 3d^{10}$ forbidden transition of the substitutional Cu⁺ ion in several alkali halides are reported. From a detailed study of the temperature dependence of τ and the comparison with the known data on the temperature variation of the oscillator strength, $f(T)$, it is concluded that the position in the lattice of Cu⁺ in the relaxed excited state and in the ground state may or may not be the same. In particular, it should be the same in the alkali iodides and NaCl, but different in the alkali bromides and KCl and RbCl.

I. INTRODUCTION

In recent years there has been considerable attention given to the change in ionic and electronic

properties in crystals in which substitutional impurity ions occupy “off-center” positions. A quite comprehensive review, with complete references, has been written by Smoluchowski.¹