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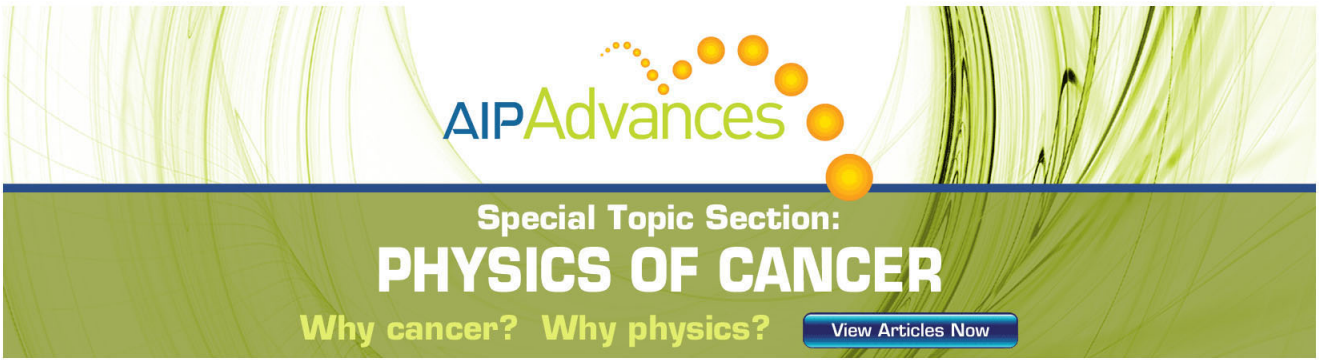
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Optical properties of *p*-GaSe single crystals doped with Te

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Optical absorption in the region of fundamental absorption edge and photoluminescence (at 78 and 293 K) of *p*-GaSe crystals doped with Te (0.05, 0.10, and 0.05 at. %) have been studied. At low concentrations (0.05 at. %), Te atoms liquidate structural defects in GaSe single crystals and modify their excitonic absorption and photoluminescence. For increased concentrations of 0.10 and 0.50 at. %, Te creates impurity states responsible for the red shift of the fundamental absorption edge of GaSe and appearance of new photoluminescence bands, B (at 2.000 eV) and C (at 1.700 eV). The activation energies of the thermal quenching of Te-related PL bands *B* and *C* was found to be 28 and 32 meV (for $T<150$ K) and 84 and 62 meV (for $T>150$ K), respectively. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3068464]

I. INTRODUCTION

III-VI layered semiconductors appear to offer an interesting and yet largely unexplored opportunity for both fundamental scientific research and technological applications.[1–3] Due to their specific quasibidimensional structure, III-VI compounds show large anisotropic properties,[4] strong excitonic emission, and large optical nonlinearity, which make them very promising candidates for future optoelectronic and photoelectronic materials.[1]

Gallium monoselenide (GaSe) is a typical member of the III-VI semiconductor group. Its layers are composed of planar packages of two selenium and two gallium sublayers in the sequence of Se–Ga–Ga–Se.[5] Also, it shows a hexagonal network with the optical axis (C_6) perpendicular to the chalcogen atomic plane.[6] In each pair of atomic planes, the Ga atom is covalently bound with three Se atoms. The chemical bonding between four monoatomic sheets inside a package has an ionic-covalent nature, whereas it is comparatively weak between packages, of Van der Waals type.[7] Due to chemical bonding anisotropy, the impurity atoms occupy less vacancies within the stratified packages, they rather locate between chalcogen atomic planes (intercalation), contributing to the formation of new valence bonds.

Thanks to its attractive properties, among which are large absorption coefficient, remarkable photoconductivity in the vicinity of the fundamental absorption edge, and large band-gap,[8] GaSe is regarded as a perspective material for different technological applications: devices for radiation generation/detection in midinfrared,[9] terahertz[10] and microwave[11] ranges, nonlinear optics,[12] solar energetics,[13] as well as a passivation layer,[14] and phase-change recording medium.[15]

GaSe is known as a semiconductor showing direct optical transitions with formation of excitonic series at low temperatures.[16] The optical properties of GaSe single crystals and thin films, doped with Cu and Mn, the covalence radii of which are greater than that of Ga, have been examined in Refs. 17 and 18. It was demonstrated that both Cu and Mn create shallow acceptor levels within the forbidden band of GaSe. In Ref. 19, spectral characteristics of photoconductivity and photoluminescence (PL) of GaSe crystals with Se excess, as well as 0.1 at. % Te-doped, were studied.

GaSe and GaTe form solid solutions, $GaSe_xTe_{1-x}$, based on the hexagonal GaSe lattice, for concentration (x) in the range $0.6 \leq x \leq 1$.[20] The absorption spectra of mentioned crystals are characterized by the presence of the free exciton absorption bands. The peak energy of the excitonic line $n=1$ at $T=78$ K linearly decreases with concentration in the range $0.72 \leq x \leq 1$.[21]

In our previous papers,[5,8,22–24] we investigated the optical, photoelectrical, and PL properties of Cu-, Cd-, Sn-doped, and fullerene-intercallated GaSe single crystals and thin films, as well as of GaS(Cu) single crystals.[25,26]

In this paper we extend previous investigations to the study of optical absorption and PL of GaSe(Te) single crystals in the temperature range of 78–293 K. A systematic investigation of the influence of low level Te-doping ($\leq$0.5 at. %) on the absorption and PL spectra of GaSe single crystals has not been carried out so far.

II. EXPERIMENTAL DETAILS

The GaSe single crystals were grown from melt (Bridgman method) by using their chemically pure component elements, Ga(4N) and Se with 99.999% purity, in stoichiometric proportions. Te doping with concentrations 0.05, 0.10, and 0.50 at. % was achieved during chemical synthesis of GaSe. From bulk single crystals plan-parallel layers with a thickness ranging between 23 and 78 μm have been splitted.

For all examined samples, the Seebeck coefficient was positive, indicating a *p*-type electrical conductivity, e.g., holes are predominant charge carriers in both undoped and

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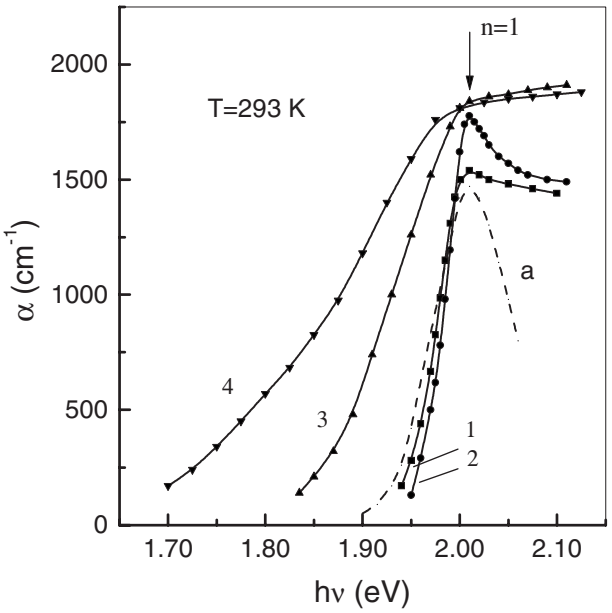


FIG. 1. Absorption spectra at $T=293$ K for GaSe single crystals: 1-undoped, 2–0.05 at. % Te-doped, 3–0.10 at. % Te-doped, and 4–0.50 at. % Te-doped. a-$\alpha(h\nu)$ curve, calculated from Eq. (1) for $\mu=0.145m_0$, $R_0=21$ meV, and $f_{CV}=0.05$.

Te-doped crystals. The absorption and PL spectra of GaSe crystals have been recorded at 78 and 293 K by a spectrophotometric setup, including a monochromator with a diffraction grating (600 mm^{-1}).

In PL measurements sample excitation was performed by an N_2 laser ($\lambda=337$ nm) at higher exciting levels, and a DRS-500 filtered mercury lamp (by using a monochromator with prism made of K-8 type glass; $\lambda=546.1$ nm) at lower exciting levels. The intensity of the exciting light was varied by using neutral density filters (thin Pt films onto amorphous SiO_2).

III. RESULTS AND DISCUSSION

In Fig. 1 absorption spectra at room temperature ($T=293$ K) of undoped (curve 1) and Te-doped (with concentrations 0.05, 0.10, and 0.50 at. %) GaSe single-crystal samples are presented. The fundamental optical absorption edge of a semiconductor single crystal, in the presence of direct exciton transition, is described by[27]

$$\alpha^*(h\nu)=\frac{(2\mu)^{3/2}e^2f_{CV}}{n_0c\hbar^2m_0}\left[\sum_n\frac{4\pi R_0^{3/2}}{n^3}\delta(h\nu-h\nu_n)+\frac{2\pi R_0^{1/2}U(h\nu-E_g)}{1-\exp(-2\pi Z)}\right], \quad (1)$$

where μ denotes the reduced exciton mass, e is elementary charge, f_{CV} is the oscillator strength associated with band-to-band transitions, n_0 is the refractive index, c is the speed of light in vacuum, m_0 is the rest mass of the electron, $h\nu_n$ is the photon energy corresponding to the excitonic state n ($n=1,2,3,\ldots$ is the excitonic quantum number), R_0 is the binding energy of the electron-hole pair, Z is equal to $[R_0/(h\nu-E_g)]^{1/2}$, and E_g is the width of the forbidden band; U is expressed by[28]

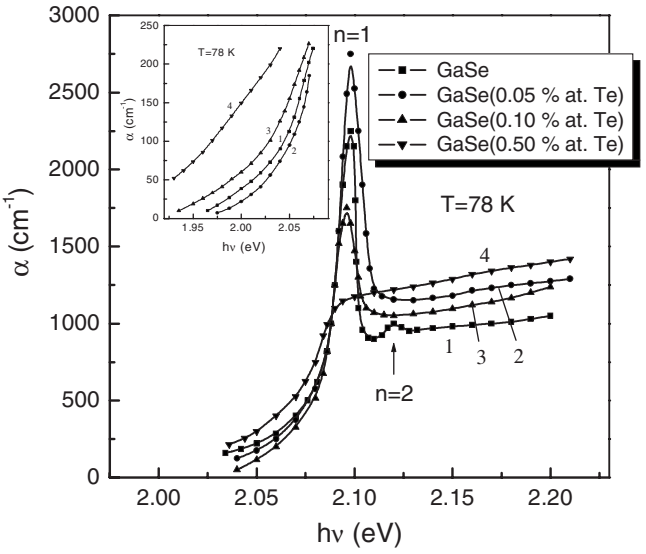


FIG. 2. Absorption spectra at $T=78$ K for GaSe and GaSe (Te) single crystals: 1-undoped GaSe, 2-GaSe (0.05 at. % Te), 3-GaSe (0.10 at. % Te), and 4-GaSe (0.50 at. % Te). Inset: the region of the fundamental absorption edge.

$$U(h\nu-E_g)=\frac{1}{\pi}\left\{\frac{\pi}{2}+\left[\arctan\left(\frac{h\nu-E_g}{\Gamma_c}\right)\right]\right\}, \quad (2)$$

with Γ_c as the full width at half maximum of the excitonic continuum states.

For GaSe single crystals, the dashed line in Fig. 1(a) is the $\alpha(h\nu)$ curve, calculated from Eq. (1) for $\mu=0.145m_0$, $R_0=21$ meV,[29] and $f_{CV}=0.05$.[30] The absorption maximum at 2.03 eV ($T=293$ K) and the continuum it further exhibits are produced by $n=1,2,3,\ldots$ excitonic transitions.

The presence of 0.05 at. % Te impurity atoms leads to enhancement of the excitonic absorption and a slow increase in the slope of the low energy part of the absorption band. Higher Te impurity concentrations (0.10 and 0.50 at. %) result in the red shift of the absorption edge, as can be seen in curves 3 and 4 (Fig. 1). Besides, an increase in the absorption coefficient at photon energies $h\nu>h\nu_{n=1}$ is registered. For this Te doping range, the defect concentration in GaSe crystals at 293 K is large enough to enable shielding of electron-hole Coulomb interaction and leads to a decrease in the intensity of the $n=1$ excitonic absorption band.

The optical absorption spectra at 78 K are illustrated in Fig. 2. In the spectrum of undoped GaSe crystals, the intense excitonic lines $n=1$ ($h\nu_1=2.099$ eV) and $n=2$ ($h\nu_2=2.118$ eV) are displayed. In the frame of the Wannier–Mott exciton theory, the energy of the excitonic line is expressed by[31]

$$h\nu_n=E_g-R_0/n^2. \quad (3)$$

By using the above equation for the excitonic lines $n=1$ and $n=2$, the band gap $E_g=2.124$ eV and the binding energy of the electron-hole pair, $R_0=26$ meV, for undoped GaSe crystals were determined.

The absorption coefficient in the center of the $n=1$ excitonic line is seen to increase from 2300 cm^{-1}, for undoped GaSe single crystal, to 2800 cm^{-1}, for 0.05 at. % Te concentration. At the same time, the absorption line $n=1$ in Te-

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doped crystals shows a broadening tendency toward higher energy region and practically is seen to overlap with the $n=2$ line, which is clearly highlighted in the stoichiometrical GaSe crystals. These results can be explained if one admits that despite Te covalence radius (1.36 Å), greater than in the case of Se (1.16 Å) and Ga (1.26 Å), Te atoms (at low concentrations) fill up Se and Ga vacancies, thus contributing to an increased probability of exciton formation through light absorption.

At doping concentrations of 0.10 at. % Te, the intensity of the excitonic line $n=1$ in GaSe is seen to decrease to 1800 cm^{-1} and this line is practically totally attenuated at 0.50 at. % Te concentration. Therefore, we can consider that at low Te doping concentration, a part of Te atoms liquidates native structural defects in the metal sublattice of hexagonal GaSe crystals, but at increased concentrations, $c \geq 0.10$ at. %, Te impurity atoms, with greater covalence radius in comparison to Ga and Se, localize in the interlayer spaces, and mainly between chalcogen layers, kept together by weak van der Waals forces. The impurity states created by Te atoms are responsible for an increased absorption of GaSe samples in the spectral range $h\nu < 2.05$ eV, where the absorption coefficient is close to 200 cm^{-1} (inset of Fig. 2, line 4).

Figure 4 shows the PL spectra at 78 K for both undoped (curve 1) and Te-doped (curves 2–4) GaSe single crystals. In the spectrum of undoped crystals the emission line peaked at 2.099 eV is seen to prevail; it coincides with the excitonic absorption line $n=1$ at this temperature (Fig. 2). At the same time, the low-energy tail of the excitonic line merges with the low intensity band B ($h\nu=2.000$ eV), which is determined by the contribution of structural defects in GaSe single crystal.[28] At photon energies lower than that of PL band of localized excitons, a similar PL band at $h\nu=2.036$ eV has been reported in Ref. 19 for both GaSe crystals with Se excess and 0.1 at. % Te-doped.

At reduced concentrations (0.05 at. %), Te impurity atoms lead to an enhancement (by ~3 times) of PL band B and appearance of a new emission band (C) in the red spectral region, with maximum at 1.700 eV. A similar PL band has also been reported in Ref. 32 for GaSe crystals, the surface of which contained microscopic defects and dislocations. As was stated in Ref. 19, the PL band by 1.7 eV (at $T=78$ K) is of impurity nature (Te dopant engendered). As can be ascertained from the comparison of curves 2–4 (Fig. 3), the intensity of the new band increases together with Te-doping concentration.

The intensity of the excitonic luminescence band (A) is seen to slightly increase (by 1.2 times) in the case of GaSe (Te-0.05 at. %) crystals, in comparison with undoped samples. This increase can be associated with the structural defect recovery through their completion with Te impurity atoms, resulting in a decreased defect concentration. The liquidation of native defects in the GaSe network by Te impurity atoms is also responsible for the increment of the absorption coefficient in the center of the excitonic absorption line (Fig. 2). However, because of noncoincidence between covalent radii of Te and those of Se and Ga, the deformations of the crystal lattice induced by substitutional atoms lead to the

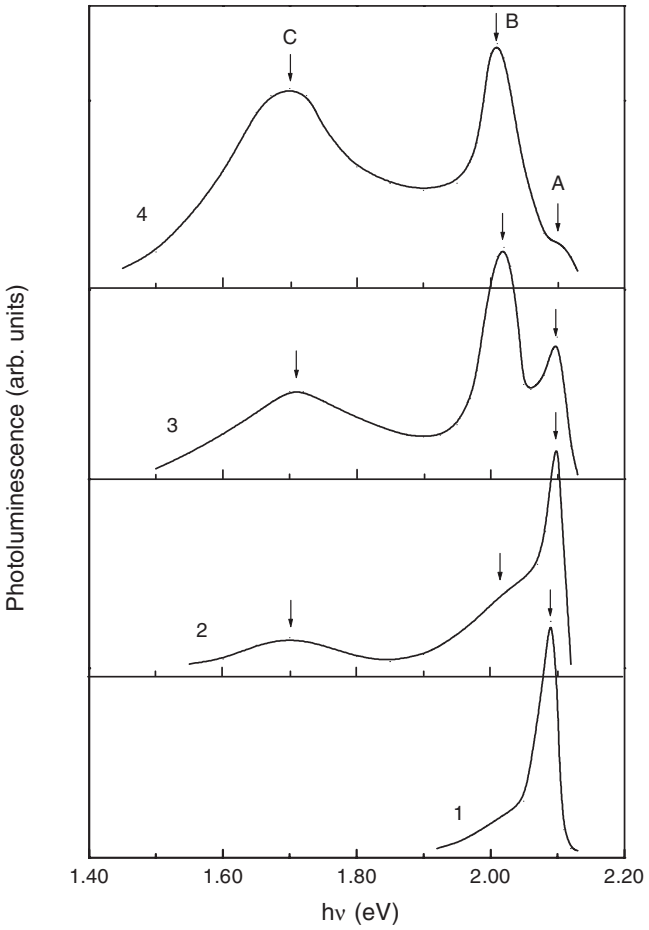


FIG. 3. PL spectra at 78 K of undoped (curve 1) and Te-doped GaSe (curves 2–4): 2–0.05 at. %, 3–0.10 at. %, and 4–0.50 at. %. Exciting power density is ~17 W/cm^2.

widening of the absorption (Fig. 2) and PL excitonic bands, as can bee seen in Fig. 3 (curve 3). At higher doping concentrations with Te (0.50 at. %), the density of related localized states is large enough to allow shielding of electron-hole Coulomb bonds, leading to strong diminution of PL exciton band A (Fig. 3, curve 4).

The bands B and C (Fig. 3) appear only in Te-doped crystals and because their intensity is increasing with impurity concentration, it is natural to suppose that they are related to the impurity levels introduced by Te atoms within the band gap of GaSe.

In order to further investigate the nature of PL bands B and C, the dependences of PL intensity (L) of the respective bands on exciting density (Fig. 4) and temperature (Fig. 5) have been examined. As can be ascertained from Fig. 4 in an interval of over two orders of magnitude of exciting radiation density (W), the $L(W)$ dependences of bands B and C can be described by a power law

$$L \propto W^p, \tag{4}$$

where the exponent p characterizes the features of the luminescence kinetics. As can be found from Fig. 4, the power coefficient p is equal to unity in the case of band B and to 0.95 for band C. The obtained values indicate that PL emission in GaSe (Te) single crystals is of monomolecular type.

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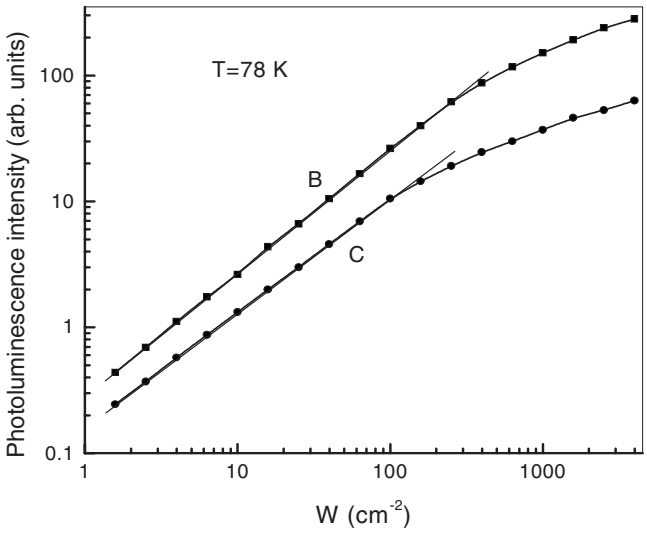


FIG. 4. Variation of PL intensity L for bands B and C of GaSe (0.5 at. % Te) against excitation power density W.

This recombination center is also responsible for the light absorption at energies lower than $h\nu_n=1$ (Figs. 1 and 2).

The intensities of PL bands B and C are seen to decrease when sample heating from 78 K is performed. For the first-order recombination kinetics, the temperature dependence of PL intensity $L(T)$ is described by[28]

$$L(T) = L(0)[1 + \alpha \exp(-E_a/kT)]^{-1}, \quad (5)$$

where $L(0)$ denotes the PL intensity at temperature $T=0$ K, E_a is the activation energy of thermal quenching of respective PL band, α is constant depending on the compound nature, and k is Boltzmann's constant. As can be observed from Fig. 5, the $L(T)$ dependence of band B obeys Eq. (5). From

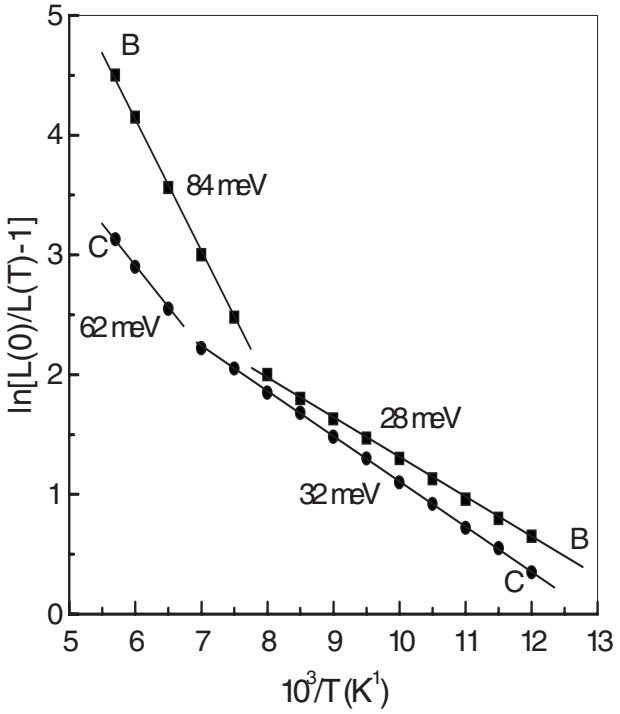


FIG. 5. Temperature dependence of PL intensity for bands B and C of GaSe (0.5 at. % Te) single crystals.

the slope of $\ln[L(0)/L(T)-1]=f(10^3/T)$ characteristics the value of E_a can be calculated. In this way, we found 28 meV for the temperature range 78 K $\leq T \leq$ 125 K and 84 meV for $T>125$ K. The obtained values are in good accordance with the reported[19] Te-created acceptor level energies of 20 and 84 meV, within the forbidden gap of GaSe, determined by the temperature dependence of the hole concentration.

The mechanism of thermal quenching of PL band C is also described by Eq. (5), with an activation energy of 32 and 62 meV for the temperature ranges of 78–150 and $T>150$ K, respectively (Fig. 5).

As was stated in Ref. 29, Te impurity atoms engender two acceptor levels in the band gap of GaSe crystals: a deep acceptor level with the energy of 84 meV and a shallow one with an energy of 20 meV. By comparing the energy values of the deep acceptor level, as determined from the temperature dependence of hole concentration[19,29] and $L(T)$ dependence, one can conclude that the luminescence emission in band B occurs through the acceptor level localized at 84 meV above the valence band.

IV. CONCLUSION

For low Te-doping levels (0.05 at. %), the native structural defects of GaSe are liquidated, leading to an increased intensity of the excitonic absorption band $n=1$. At higher impurity concentrations, Te atoms engender energy states within the GaSe band gap, resulting in an absorption enhancement in the range of $h\nu<2.05$ eV and formation of two PL bands at 2.000 eV (band B) and 1.700 eV (band C) of monomolecular nature.

The thermal quenching of band B is characterized by two activation energies, 28 and 84 meV, for temperature ranges 78 K $\leq T \leq$ 125 K and $T>125$ K, respectively. For band C the activation energy was found to be 32 and 62 meV for temperature in the ranges 78–150 K and $T>150$ K, respectively.

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