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Direct excitation of Tl^+ impurity ions by hot photoelectrons in wide-gap crystals

E. Feldbach
Institute of Physics, Riia 142, EE2400, Tartu, Estonia

M. Kamada
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

M. Kirm
Institute of Physics, Riia 142, EE2400, Tartu, Estonia

A. Lushchik
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan
and Department of Physics, Tartu University, Tähe 4, EE2400, Tartu, Estonia

Ch. Lushchik
Institute of Physics, Riia 142, EE2400, Tartu, Estonia

I. Martinson
Department of Physics, Lund University, Sölvegatan 14, S-22362 Lund, Sweden

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The reflection spectra of KCl and RbCl crystals and excitation spectra of *A* and *B* luminescence and recombination phosphorescence of Tl^+ centers for RbCl:Tl and KCl:Tl crystals have been measured in a spectral region from 5 to 30 eV. The energy distribution curves of emitted electrons have been measured on the excitation of RbCl thin films by 13–30 eV photons. The comparative analysis of optical and photoelectric characteristics allowed us to reveal the effect of direct excitation of Tl^+ impurity ions up to $A(^3P_1)$, $B(^3P_2)$, and $C(^1P_1)$ states by hot conduction electrons. The threshold photon energies of this effect are determined. The estimated energies of conduction electrons, formed by such photons, are close to the energies of direct optical transitions $^1S_0 \rightarrow {}^3P_1$ (5 eV) and $^1S_0 \rightarrow {}^3P_2$ (6 eV) of Tl^+ centers in KCl:Tl and RbCl:Tl crystals. Similar to the case of ns^2 free atoms, the excitation functions for triplet states of Tl^+ centers have a sharp maximum at the energy just above the threshold in RbCl:Tl and KCl:Tl crystals. The peculiarities of electron impact spectroscopy of impurity ions in wide-gap crystals are discussed. [S0163-1829(97)02045-6]

I. INTRODUCTION

The effect of multiplication of electronic excitations (MEE's), when one absorbed photon creates several electronic excitations (EE's) in a crystal, was revealed for semiconductors long ago.[1] MEE is caused by energetic (hot) conduction electrons that create secondary electron-hole (e-h) pairs. For narrow-gap crystals the existing theories of secondary e-h pair creation, due to the interband impact or Auger mechanisms, are in good agreement with experimental results.[2]

MEE processes are investigated for wide-gap metal halide and oxide crystals ($E_g = 6-12$ eV) by means of luminescence[3–7] and photoelectric[8–11] methods. The excitonic mechanism of MEE which involves the creation of secondary excitons (SE's) by hot photoelectrons (HPE's) occurs in dielectrics with excitons of medium and small radii (see Ref. 7, and references therein).

The third MEE mechanism, connected with inelastic scattering of hot conduction electrons and excitation of impurity ions, can take place in crystals doped by luminescent impurity ions. The threshold energy of this mechanism can be significantly smaller than that of excitonic or e-h mechanisms of MEE's in wide-gap crystals. The manifestations of Mn^{2+} ion excitation by HPE's at a significantly lower exciting photon energy than the threshold energy for e-h pair multiplication have been observed in a ZnS:Mn crystal ($E_g = 3.7$ eV) with a high concentration of Mn^{2+} ions.[12] In wide-gap crystals doped with various impurity ions, the expected effect of impurity ion excitation by HPE's has not been revealed until recently. The application of synchrotron radiation (SR) allowed us to initiate the investigation of Tl^+ ion excitation by HPE's in a KBr:Tl crystal.[5] However, the necessity to distinguish the direct excitation of Tl^+ centers by HPE's from the excitonic and e-h excitation mechanisms of luminescent Tl^+ ions impeded the quantitative study of this effect. The coexistence of free and self-trapped EE's with the energy states separated by an activation barrier causes the effective excitation of Tl^+ due to the excitonic and e-h mechanisms in alkali bromide and iodide crystals at low temperature.[13]

The aim of the present study is to select and quantitatively investigate the process of Tl^+ center excitation by HPE's in RbCl and KCl crystals. In these crystals the process of exciton self-trapping is very rapid even at low temperatures and therefore the efficiency of the excitonic mechanism of Tl^+

luminescence is extremely low.[14] At temperatures $T<200$ K, the hopping diffusion of self-trapped holes is frozen also, so the e-h mechanism of impurity luminescence is ineffective as well because of a small mean free path of hot holes before their self-trapping in RbCl and KCl.[14]

Electron impact spectroscopy of free atoms and ions is elaborated in detail (see, e.g., Ref. 15). On the other hand, the spectroscopy of impurity ions, which substitute cations and anions in a crystal, is still poorly investigated. Single attempts to excite impurity ions in wide-gap crystals by a low-energy electron beam (see, e.g., Ref. 16) met experimental difficulties caused by a small depth of 5–50 eV electron penetration into near-surface layers of a crystal. The use of monochromatic SR enabled us to easily create hot conduction electrons, the energy of which is sufficient to excite Tl$^+$ impurity ions in a crystal. The parallel investigation of energy distributions of electrons emitted from a RbCl thin film allowed us to estimate quantitatively the kinetic energy of conduction electrons sufficient enough for Tl$^+$ excitation up to various states.

II. EXPERIMENTAL

The photoluminescence experiments were carried out at beamline 52 in the MAX Laboratory in Lund, Sweden (550 MeV storage ring). The samples were mounted in a cold-finger helium cryostat (8–300 K). SR was focused onto a crystal through a 1-m normal-incidence monochromator (4–32 eV) with a typical optical slit width of 0.24 nm. A LiF filter was inserted into the optical path of the incident SR during measurements below 10 eV. The luminescence from a sample was analyzed using a second 0.3-m-grating monochromator (perpendicular to incident SR direction) and photomultiplier Hamamatsu R585 operating in the photon counting mode. The emission spectra were corrected for the monochromator transmittance and the sensitivity of the photomultiplier. The reflection spectra for the (100) plane of RbCl were measured at an angle of 45° after a crystal cleavage *in situ* under ultrahigh-vacuum conditions (10^{-9} mbar). The excitation spectra were measured at incidence angle of 25° and a typical optical slit width of secondary monochromator 10 nm. The reflection and excitation spectra were normalized to equal quantum intensities of the excitation falling onto the crystal. The reference signal for normalization was recorded from a sodium-salicylate coated mesh.

The photoelectron spectra were measured at beam-line 6A2 in the UVSOR facility in Okazaki, Japan (750 MeV storage ring). A RbCl thin film with a thickness about 100 Å was evaporated on a gold-coated substrate. The photoelectrons from the RbCl film were analyzed using a homemade cylindrical retarding field energy analyzer.[17] The plane grating monochromator with changeable focusing mirrors was used to obtain the monochromatic exciting light of 13–30 eV. The intensity of incident light was monitored by a gold mesh located between a post-mirror and a sample. All spectra are normalized by using photoelectric yield of this gold mesh. All energy distribution curves of the emitted electrons were measured at room temperature in ultrahigh vacuum of 10^{-9} mbar. No significant effects of surface charging were observed.

Cubic face-centered RbCl and KCl crystals of high purity as well as crystals doped with Tl$^+$ impurity ions (RbCl:Tl and KCl:Tl) were the main objects of the present study. Single RbCl and KCl crystals were grown by the Stockbarger method from the salts after a special purification cycle involving a melt treatment in Cl_2 gas flow and a 50-fold recrystallization from the melt. The content of impurity ions was on the level of 0.01–3 ppm. Only the concentration of K^+ in RbCl was about 100 ppm. The content of Tl$^+$ ions in a doped crystal was estimated by means of optical methods and is given in parentheses: RbCl:Tl (200 ppm) and KCl:Tl (300 ppm).

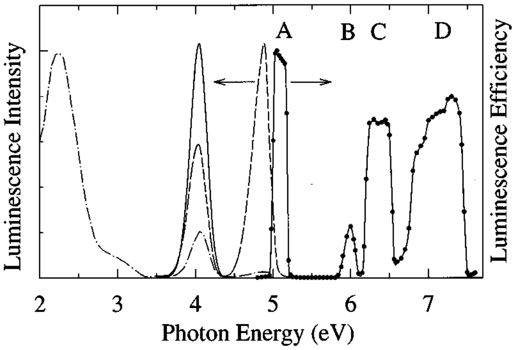

FIG. 1. The excitation spectrum of A emission of Tl$^+$ centers (●) and the emission spectra of a RbCl:Tl crystal on the excitation by 5.05 eV (solid line), 6.0 eV (dashed line), and 7.62 eV (— · —) photons. All spectra are measured at liquid-helium temperature.

III. PHOTOEXCITATION AND IONIZATION OF Tl$^+$ CENTERS IN RbCl:Tl AND KCl:Tl

The first interpretation of Tl$^+$ center absorption spectra in alkali-halide crystals as ${}^1S_0\rightarrow{}^3P_1$, ${}^1S_0\rightarrow{}^3P_2$, and ${}^1S_0\rightarrow{}^1P_1$ electron transitions of Tl$^+$ perturbed by crystal lattice[18] was later specified and applied to a large group of ‘‘mercury-like’’ ions with ns^2 ground-state configuration (Ga$^+$, In$^+$, Tl$^+$, Ge^{2+}, Sn^{2+}, Pb^{2+}).[19] Unfortunately, Tl$^+$ centers in RbCl:Tl have been poorly investigated up to now.

Figure 1 presents the excitation spectrum of A emission (the maximum $E_m=4.03$ eV, half-width $\delta=0.24$ eV) of Tl$^+$ centers measured in the region of 4.7–8.0 eV for RbCl:Tl at 4.2 K. The A, B, and C excitation maxima (5.1, 6.0, and 6.35 eV) correspond, respectively, to ${}^1S_0\rightarrow{}^3P_1$, ${}^1S_0\rightarrow{}^3P_2$, and ${}^1S_0\rightarrow{}^1P_1$ electron transitions of a free Tl$^+$ ion, or to ${}^1A_{1g}\rightarrow{}^3T_{1u}$, ${}^1A_{1g}\rightarrow{}^3T_{2u}$, ${}^3E_u$, and ${}^1A_{1g}\rightarrow{}^1T_{1u}$ transitions in the crystal field of cubic symmetry (Tl$^+$ substitutes a host Rb$^+$ ion). The B emission ($E_m=4.9$ eV, $\delta=0.25$ eV) of Tl$^+$ centers cannot be excited within the A excitation (absorption) band, while its excitation efficiency is high in the region of B, C, and D absorption bands. In contrast to A, B, and C bands, D absorption bands are not associated with direct optical excitation of Tl$^+$ from $6s^2$ to the $6s6p$ configuration, but are caused by the excitation and ionization of Cl$^-$ ions surrounding the impurity ion.[19] The excitation of KCl:Tl or RbCl:Tl in the region of a nonelementary D band leads to the appearance of A and B emissions (radiative transitions ${}^3P_1\rightarrow{}^1S_0$ and ${}^3P_2\rightarrow{}^1S_0$, respectively) of Tl$^+$ ions as well as typical D emission ($E_m=2.5$ eV in RbCl) which is caused by the recombination of electrons with Cl_2^- quasimo-

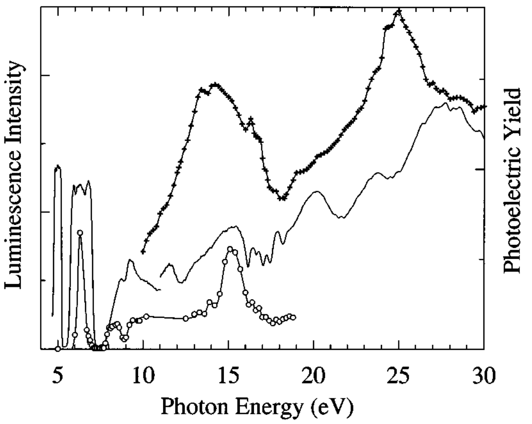

FIG. 2. The excitation spectra of steady A emission (solid line) and recombination phosphorescence (○) of Tl^+ centers in a RbCl:Tl crystal at 295 K. The spectrum of photoelectric yield (×) for a RbCl thin film at 295 K (Ref. 9).

lecules forming after relaxation of Cl^0 centers.[14] In a RbCl:Tl crystal D bands adjoin directly the exciton absorption bands. The direct optical formation of excitons by 7.62 eV photons is responsible for the appearance of the well-studied 2.23 eV emission of self-trapped excitons[20] (STE's) and weak A emission of Tl^+ centers. The efficiency of A emission caused by exciton energy transfer to impurity centers is by an order of magnitude lower than that of STE luminescence (see Fig. 1). Our experimental estimates showed that the quantum yield of STE luminescence in RbCl:Tl and KCl:Tl does not exceed 0.05 at 4–10 K and sharply decreases at higher temperatures.[14,20] At the same time the quantum yield of A emission is close to unity on direct optical excitation of Tl^+ within the A absorption band. So, the efficiency of the excitonic mechanism of Tl^+ luminescence excitation is about 0.005 in a RbCl:Tl (200 ppm) crystal.

Figure 2 shows the excitation spectrum of A emission of Tl^+ centers measured for RbCl:Tl at room temperature. The efficiency of A luminescence η_A is close to unity in the region of A, B, C, and D bands ($h\nu \leqslant 7$ eV), is on the noise level in case of direct exciton formation and starts to increase at $h\nu > 8.2$ eV where photons form at 295 K separated electrons and holes (e-h pairs). At 10 eV η_A exceeds 0.4, i.e., about half of e-h pairs recombine at Tl^+ centers producing impurity luminescence. At 295 K, mobile holes interact with Tl^+ thereby forming Tl^{2+} centers. The recombination of an electron with Tl^{2+} takes the place via an excited state of Tl^+. A subsequent radiative transition to the ground state of Tl^+ then takes place. The cooling of RbCl:Tl down to 200 K freezes the hopping diffusion of the relaxed two-halide holes (V_K centers) and decreases the value of η_A by 6 times. However, Tl^{2+} centers still arise at $T < 200$ K due to the migration of hot (nonrelaxed) holes, the mean free path of which before self-trapping is about 10 lattice constant.

Figure 2 also depicts the excitation spectrum of Tl^+ phosphorescence. The intensity of Tl^+ A emission, detected 3 s after the end of excitation, was taken as a measure of this phosphorescence caused by the recombination of electrons with Tl^{2+} formed on the partial thermal ionization of excited Tl^+ centers (see details in Ref. 21). The ${}^1S_0 \rightarrow {}^3P_1$ transitions practically do not lead to Tl^+ ionization, while ${}^1S_0 \rightarrow {}^3P_2$ and especially ${}^1S_0 \rightarrow {}^1P_1$ transitions cause a partial ionization of Tl^+.

Recently the process of MEE has been studied in a RbCl crystal of high purity at 8 K.[6] Measuring the spectrum of STE luminescence (2.23 eV) excitation by SR, the threshold photon energies for the formation of secondary excitons or e-h pairs by HPE's (16 and 18 eV, respectively) have been determined. According to Fig. 2 the value of η_A doubles if the exciting photon energy increases from 10 to 12 eV, when one photon produces only one e-h pair, to $h\nu = 18–20$ eV, when a photon forms two e-h pairs. The next sharp increase of the efficiency of A emission of Tl^+ takes place at $h\nu \approx 28$ eV. In this region the value of η_A is higher than in the region of direct optical excitation of Tl^+ centers (A, B, C absorption bands). Even taking into account the energy losses during an e-h pair migration to a Tl^+ center the quantum yield of photoluminescence η_A exceeds unity at $h\nu \approx 28$ eV. This is the effect of photon multiplication observed earlier in a number of alkali-halide crystals.[3,7]

This e-h process of MEE gets complicated in RbCl:Tl because of several phenomena. In Fig. 2 we reproduce the spectrum of photoelectric yield η_j measured by Eijiri, Hatano, and Nakagawa[9] in the region of 10–30 eV for a RbCl thin film at 295 K. The sharp decrease of η_j at 17.0–19.5 and 28–29 eV is ascribed to the formation of secondary e-h pairs by HPE's.[9] However, the value of η_j decreases in the regions of 16–17 and 26–27 eV also. In our opinion the formation of SE's by HPE's takes place just in these regions. The effect of SE formation will be discussed below, after the presentation of our original photoelectric data.

There is a group of five minima at 16.0–18.5 eV in the excitation spectrum of Tl^+ luminescence for RbCl at 295 K. These minima correlate with the reflection and absorption maxima which were convincingly interpreted as the formation of cation excitons $-4p^5 5s^1$ and $4p^5 4d^1$ excitations of Rb^+ ions.[22,23] After correction of the excitation spectrum for reflection losses ($R \leqslant 15\%$ in the region of 16.0–18.5 eV),[22] the depths of the minima decrease while the minima still remain. There is a clear correlation between the absolute value of the absorption constant and the above-mentioned excitation minima. For high absorption constants the penetration depth of incident radiation is low and EE's are formed only in a thin crystal layer, increasing the probability of nonradiative e-h recombination at the surface and therefore decreasing the efficiency of Tl^+ luminescence.

IV. EXCITATION OF Tl$^+$ CENTER LUMINESCENCE BY CONDUCTION ELECTRONS IN A RbCl:Tl CRYSTAL

In the present study we pay special attention to the excitation of A emission of Tl^+ centers in the regions of 13–16 and 22–25 eV. HPE's formed by 13–16 eV photons are not able to create SE's or secondary e-h pairs. There is a strong maximum at 14–16 eV in the excitation spectrum of Tl^+ recombination phosphorescence (see Fig. 2). The analogous maximum at 6.0–6.7 eV was ascribed to a partial ionization of Tl^+ centers excited up to B and C states.[21] Photons of $h\nu \geqslant 14.5$ eV create HPE's which excite Tl^+ centers up to the $C({}^1P_1)$ state at 295 K. A part of these excited Tl^+ undergoes ionization. As a result, a recombination phosphores-

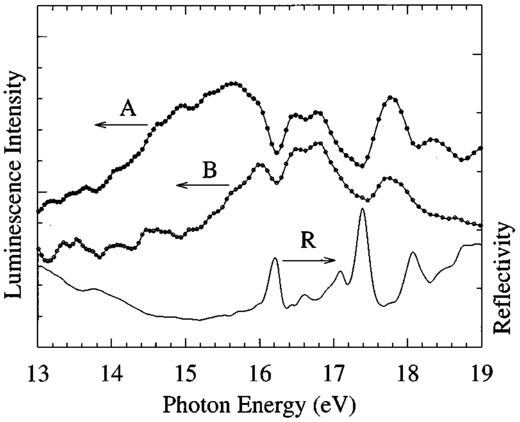

FIG. 3. The excitation spectra of Tl$^+$ emissions at 4.03 eV (A emission) and 4.9 eV (B emission) in a RbCl:Tl crystal at 8 K. The reflection spectrum (R) for a RbCl crystal at 8 K.

cence of Tl$^+$ appears in RbCl:Tl at 295 K. The temperature decrease leads to the disappearance of Tl$^+$ phosphorescence because the ionization process of excited Tl$^+$ becomes frozen. In KCl:Tl the situation is similar—there are two main maxima (6.4 and 16 eV) in the spectrum of Tl$^+$ recombination phosphorescence excitation at 295 K.[24]

Figure 3 presents the excitation spectra for A and B emissions of the Tl$^+$ center measured in the region of 13–19 eV for a RbCl:Tl crystal at 8 K. At 13–14 eV, $\eta_A \approx 0.08$ and A emission arises due to the subsequent trapping of electrons and holes by Tl$^+$ centers. The rise of A emission efficiency begins at $h\nu > 14$ eV and the value of η_A reaches 0.13. The efficiency of the weak B emission (4.95 eV) η_B stays practically constant (without taking into account reflection and near-surface losses) at 13–15 eV and sharply increases in the region of 15–16 eV. In the same region we observed the increase of Tl$^+$ phosphorescence efficiency at 295 K (see Fig. 2), which is connected with the excitation of Tl$^+$ to B and C states. The energy difference (1 eV) between regions of a sharp increase of η_A and η_B reflects the positions of A and B absorption (excitation) bands of Tl$^+$ centers (see Fig. 1).

In a RbCl crystal at 8 K, the energy gap is $E_g = 8.5$ eV,[20,25] and the total width of the valence band is 2.2 eV.[25] An s photoelectron, the effective mass of which is, in our estimation, at least ten times smaller than that of a p hole, gains the main part of the photon energy on the direct optical interband transition. Therefore, it was expected that 14 eV photons, the energy of which exceeds the value of E_g by 5.3 eV, can produce HPE's that are able to excite Tl$^+$ to the A state ($^3P_1$). The 6 eV conduction electrons with the energy sufficient to excite Tl$^+$ to the B state ($^3P_2$), can be probably formed by 15 eV photons.

We estimate that the efficiency of A emission excitation by HPE's is close to $\eta_A = 0.25$ at 295 K. At 8 K, the value of η_A decreases to ≈ 0.05 because of partial trapping of HPE's by Tl$^+$ ions with the formation of Tl^0 centers. The peak of the thermally stimulated luminescence with the maximum at 295 K is caused by the thermal dissociation of Tl^0 centers in RbCl:Tl. The recombination of electrons, thermally released from Tl^0 centers, with Tl^{2+} leads to the appearance of Tl$^+$ recombination phosphorescence at room temperature.

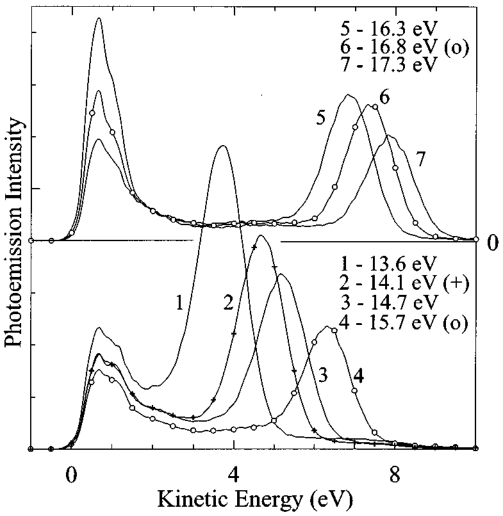

FIG. 4. EDC's of a RbCl thin film for various exciting photon energies at 295 K. Kinetic energy of the emitted electrons is measured relative to the vacuum level.

The absorption bands at 14.9 and 16.2 eV have been observed in the spectrum of fundamental absorption of TlCl and ascribed to the excitation of 5d electrons of Tl$^+$.[26] So, it is not excluded that the same excitations of Tl$^+$ can be formed at 15–16 eV in RbCl:Tl causing the increased efficiency of A emission in this region. However, the ratio of the absorption constant of Tl$^+$ in RbCl:Tl (200 ppm) and the value of intrinsic absorption of RbCl is less than 10^{-3} in the region of 15–16 eV. On the other hand, the efficiency of the process interpreted as Tl$^+$ center excitation by HPE's at 295 K is at least by 25 times higher.

According to Fig. 2 the value of the photoelectric yield does not decrease at 22.5–23.5 eV, while η_A increases at RbCl:Tl excitation by photons of such energies at 295 K. The energy of photoelectrons, formed by 22.5–23.5 eV photons, is not sufficient for the creation of secondary anion excitons or e-h pairs. In RbCl:Tl at 8 K, we observed the increase of A emission efficiency at 23 eV, while η_B starts to rise at exciting photon energy by 1 eV higher. We will show below that 22–23 eV photons effectively create HPE's with the energy of 5.0–5.7 eV sufficient for Tl$^+$ excitation up to the A state.

V. CONDUCTION ELECTRONS AND PHOTOELECTRIC EMISSION IN A RbCl FILM

In order to obtain additional information on HPE's formed by 13–30 eV photons we used photoelectric methods to investigate RbCl thin films. The energy distributions of the emitted electrons have been measured on the excitation of a RbCl evaporated film by 13–30 eV photons at 295 K. Figures 4 and 5 present some of such energy distribution curves (EDC's). The kinetic energy of the emitted electrons E_{kin} is given relative to the vacuum level. In Fig. 4 it is easy to separate two groups of emitted electrons, slow electrons with $E_{\mathrm{kin}} < 2$ eV and hot photoelectrons with linearly increasing E_{kin} at the increase of exciting photon energy $h\nu$. Photons with $h\nu = 8.4$–16.0 eV cause the ionization of chlorine ions ($3p^6$ Cl$^-$) with the formation of HPE's. A simul-

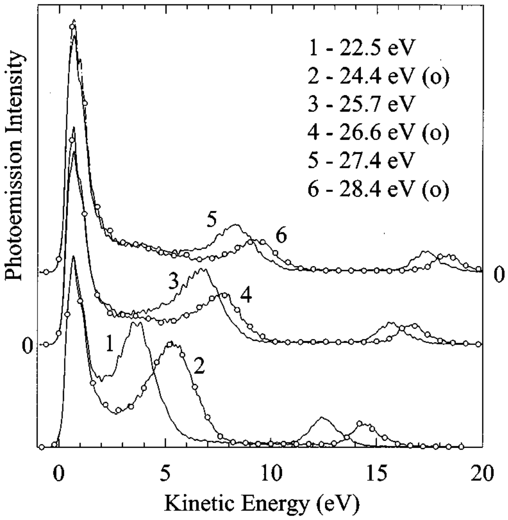

FIG. 5. EDC's of a RbCl thin film for various exciting photon energies at 295 K.

taneously formed photohole gains only a small part of the photon energy.

Besides Cl^- ionization, photons of $h\nu > 22$ eV cause the ionization of the $4p^6$ shell of Rb^+. EDC's for these exciting photon energies are shown in Fig. 5. The photoemission of the electrons with $E_{kin} > 11$ eV is caused by the photoionization of Cl^-. The photoionization of cations is responsible for the appearance of two groups of the emitted electrons, $E_{kin} < 2$ eV and $E_{kin} = 3-10$ eV. The average energy in the second group increases linearly with the rise of $h\nu$. However, if E_{kin} reaches the value of 7–8 eV, the number of fast emitted electrons significantly decreases simultaneously with the increase of the number of slow emitted electrons. The process of MEE with the formation of secondary anion excitons or e-h pairs causes such overdistribution between the number of slow and fast emitted electrons.

Figure 6 shows the dependence of the number of emitted electrons with a given E_{kin} on the exciting photon energy. The energy of conduction electrons inside a crystal is higher by a value of an electron affinity [for RbCl $\chi = 0.5$ eV (Refs. 9 and 25). There are two maxima for every value of E_{kin}, at 13–19 and 21–28 eV. The low-energy peak is caused by the ionization of chlorine ions, while the ionization of Rb^+ ions takes place in RbCl at $h\nu \geqslant 17$ eV. The distinct maximum at 16.1 eV in the absorption spectrum of RbCl was convincingly interpreted as the formation of $4p^5 5s$ Rb^+ cation exciton and a shoulder at 16.9 eV was hypothetically ascribed to the threshold of cation photoionization E_{gc}.[22] The last hypothesis was confirmed later by the investigation of crossluminescence, the emission that arises due to the radiative recombination of electrons from the halide valence band and a holes formed in the narrow $4p^5$ Rb^+ cation band. The threshold excitation energy of 5 eV crossluminescence equals $E_{gc} = 17$ eV in a RbF crystal.[27] The comparison of cation excitations in RbCl, RbBr, and RbI (Ref. 22) allows us to expect that the photoionization threshold of $4p^6$ Rb^+ in RbCl is close to the one in RbF. Unfortunately, the crossluminescence in RbCl should be located in a spectral region of 7–9 eV and should be strongly weakened due to nonradiative Auger transitions with the formation of secondary EE's. Therefore we failed to determine E_{gc} in RbCl by using the excitation spectrum of crossluminescence. The detailed study of the piezoreflectivity of RbCl crystals made it possible to conclude that $E_{gc} \approx 17.3$ eV.[28]

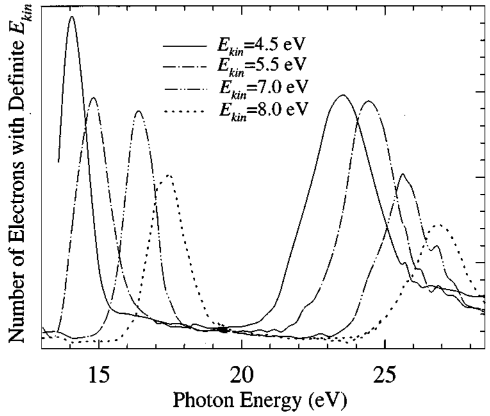

FIG. 6. Number of emitted electrons with definite kinetic energy E_{kin} as a function of exciting photon energy in a RbCl thin film at 295 K.

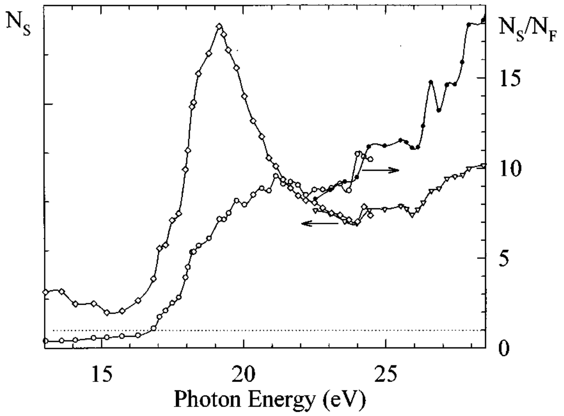

FIG. 7. The dependence of peak intensity for slow ($E_{kin} < 2$ eV) emitted electrons (◇ and ▽) and of peak intensity ratio for slow and fast emitted electrons (○ and ●) on the exciting photon energy in a RbCl thin film at 295 K.

We obtained approximately the same value of E_{gc} by means of photoelectric measurements also. Figure 7 depicts the dependence of peak intensity (number) ratio for slow ($E_{kin} < 2$ eV) and fast emitted electrons, N_s/N_f on the exciting photon energy of $h\nu = 13-30$ eV. The value of N_s/N_f is less than unity at $h\nu = 13.0-16.8$ eV, reaches $N_s/N_f = 1.05$ at 16.9 eV, and sharply increases at further rise of $h\nu$. A similar effect was earlier observed in KCl ($E_{gc} = 20.8$ eV) and interpreted as the manifestation of inelastic scattering of HPE's on valence electrons that cause the formation of secondary e-h pairs.[8] In RbCl the situation is more complicated. The sharp increase of the number of slow emitted electrons at $h\nu = 17-19$ eV (see Fig. 7) can be connected not only with the multiplication of e-h pairs, but also with the photoionization of the $4p^6$ shell of Rb^+ that produces slow s conduction electrons. With the increase of exciting photon energy at 19–24 eV the value of N_s significantly decreases—photons with higher energy produce more energetic conduction electrons. The next increase of N_s/N_f in RbCl takes place at $h\nu \geqslant 26$ eV and at $h\nu \geqslant 28$ eV because the energy of conduction electrons, formed at the photoionization of cations, becomes sufficient for the formation of secondary excitons or e-h pairs.

Our photoelectric data are in good agreement with the data obtained by luminescent methods and confirm that photoionization of anions or cations by 18–19 or 28–29 eV, respectively, leads to the appearance of 8.5 eV conduction electrons able to create secondary e-h pairs. Conduction electrons with the energy of 7.5 eV can create secondary anion excitons. The irradiation of RbCl by photons of 15.6–16.0 or 24.5–26.0 eV provides the formation of such conduction electrons.

According to Fig. 6 photons of 13.5–15.0 and 14–16 eV produce in RbCl conduction electrons with the energy of 5 and 6 eV, respectively (with respect to the bottom of the conduction band) that are close to the optical excitation energy of Tl^+ up to $^3P_1$ and $^3P_2$ states. So, these data confirm our conclusion on the excitation of Tl^+ centers by hot conduction electrons in RbCl:Tl. It is necessary to mention that the irradiation of RbCl by 22–25 eV photons leads to the appearance of 5–6 eV conduction electrons also. Our luminescent data prove the excitation of Tl^+ to A and B states on RbCl:Tl irradiation by 22–25 eV photons at 295 K. The photons with such energy are not able to create secondary e-h pairs, while they cause the increase of A luminescence efficiency (see Fig. 2). The spin-orbit splitting of the $4p^6$ shell of Rb^+ (0.9 eV),[9,22] is significantly higher than that for the $3p^6$ shell of Cl^- (0.1 eV). This is one of the reasons for peak broadening at $h\nu > 21$ eV in comparison to the peaks at $h\nu_{\mathrm{exc}} < 16$ eV (see Fig. 6). Further investigation of the influence of spin-orbit splitting on the process of Tl^+ excitation by HPE's at low temperatures is needed.

VI. MULTIPLICATION MECHANISMS OF ELECTRONIC EXCITATIONS IN RbCl:Tl AND KCl:Tl CRYSTALS

A detailed consideration of the band structure of a crystal is needed for the understanding of MEE mechanisms. The electronic structure of alkali halides has been investigated theoretically (see Ref. 29, and references therein). The first calculation of the band structure of RbCl has been done by Kunz.[30] Below we will consider only main peculiarities of the band structure in RbCl and KCl.

Figure 8 shows a simplified energy-level diagram of an alkali chloride. CVB and AVB are cation and anion valence bands, respectively, CB is a conduction band, and FB is a band of forbidden energy (energy gap). The threshold photoionization energies of anions (E_{ga}) and cations (E_{gc}) as well as the formation energies of anion and cation excitons (E_{ea} and E_{ec}) are shown in the diagram. The vacuum level is located above the bottom of CB by the value of an electron affinity χ. The energy levels, connected with the $^1S_0$ ground state and the A, B, C excited states ($^3P_1$, $^3P_2$, and $^1P_1$) of an impurity Tl^+ center or near-impurity excitations (D states) are depicted also. The numerical values of the parameters shown in Fig. 8 are presented in Table I for RbCl:Tl and KCl:Tl crystals.

The energy of HPE, formed on the photoionization of an anion or an alkali ion, can be nonradiatively transferred (waved arrows) for the formation of a secondary e-h pair (case 3 in Fig. 8) or a secondary anion exciton (case 2). If a hot conduction electron meets a Tl^+ center the latter can be excited to A, B, C, or D states. The process of Tl^+ center excitation by HPE up to A state is illustrated in the figure (case 1) as well.

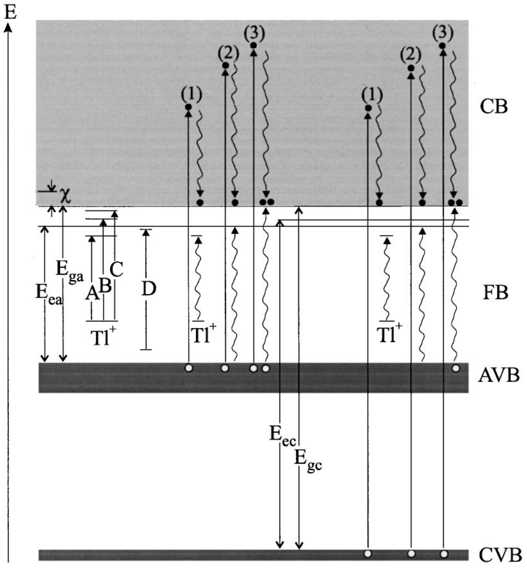

FIG. 8. Schematic energy-level diagram of an alkali chloride crystal doped with Tl^+ impurity ions. Symbols are explained in the text.

The lower part of Table I contains the experimentally determined threshold photon energies for the creation of secondary anion excitons (E_{ta}^{ex}, E_{tc}^{ex}) and secondary e-h pairs ($E_{ta}^{\text{e-h}}$, $E_{tc}^{\text{e-h}}$) as well as for the excitation of Tl^+ to A and B states (E_{ta}^{A}, E_{tc}^{A} and E_{ta}^{B}, E_{tc}^{B}) by hot conduction electrons formed due to the photoionization of $3p^6$ Cl^- anions (the lower index a, e.g., E_{ta}^{ex}) or $4p^6$ Rb^+ cations (the lower index c, e.g., E_{tc}^{B}). The main values presented in Table I were determined at 4.2–10 K. At 295 K, the values of E_{abs} for A, B, and C absorption bands decrease by less than 0.1 eV, while the value of E_{ea}, decreases by 0.3 eV. The values of threshold photon energies given in parentheses were obtained at 295 K. To compare the threshold photon energies for the formation of secondary e-h pairs at 8 and at 295 K, it is necessary to consider that anion excitons with $n=2$ undergo thermal ionization at 295 K causing an additional decrease of $E_{ta}^{\text{e-h}}$.

An analysis of the data in Table I shows that the multiplication of intrinsic EE's occurs differently in RbCl and KCl crystals. In KCl, $E_{gc} > 2E_{ga}$ in a whole temperature range and after the photoionization of $3p^6$ K^+ the Auger recombination of a cation hole and an electron from the adjacent Cl^- with the formation of two e-h pairs is possible. The numerous investigations of crossluminescence in CsCl (see, e.g., Ref. 32) confirm that $E_{gc}=14$ eV $< 2E_{ga}=16.8$ eV. So, the decay of cation excitations with the formation of a double amount of anion EE's is impossible for energetic reasons. In RbCl the situation is especially complicated. At low temperatures, $E_{gc}=17.2$ eV $> 2E_{ga}=17$ eV and the recombination of an electron from $3p^6$ Cl^- with a $4p^6$ Rb^+ cation hole can, similar to CsCl, cause the appearance of

TABLE I. Peak positions of the emission (E_{emis}) and absorption (E_{abs}) bands of Tl^+ centers (excited up to A, B, C, and D states); threshold photoionization energies of anions (E_{ga}) and cations (E_{gc}) and formation energies of anion and cation excitons (E_{ea} and E_{ec}); threshold photon energies for the creation of secondary anion excitons (E_{ta}^{ex}, E_{tc}^{ex}), secondary e-h pairs ($E_{ta}^{\mathrm{e\text{-}h}}$, $E_{tc}^{\mathrm{e\text{-}h}}$) or for the excitation of Tl^+ to A and B states (E_{ta}^A, E_{tc}^A and E_{ta}^B, E_{tc}^B) by HPE's formed due to the photoionization anions (the lower index a) or cations (the lower index c). All energy values (in eV) were obtained at 4.2–10 K or at 295 K (in parentheses).

	RbCl	KCl
E_{abs}^A	5.10 [b]	5.03 [a]
E_{emis}^A	4.03 [b]	4.15 [a]
E_{abs}^B	6.00 [b]	5.92 [a]
E_{emis}^B	4.90 [b]	5.02 [a]
E_{abs}^C	6.35 [b]	6.37 [a]
E_{abs}^D	7.15; 7.34	7.20; 7.45 [a]
E_{ea}	7.60 [c]	7.77 [c]
E_{ga}	8.5 [d]	8.7 [a]
E_{ec}	16.1 [g]	20.0 [e]
E_{gc}	17.2	20.8
E_{ta}^A	14.0 (13.5)	14.3 [f]
E_{ta}^B	15.0 (14.2)	15.3 [f]
E_{ta}^C	(14.5)	(15.3) [f]
E_{tc}^A	22.5 (22.0)	26.2
E_{tc}^B	23.0	26.7
E_{ta}^{ex}	16.0 (15.4)	16.9 [f] (16.5)
$E_{ta}^{\mathrm{e\text{-}h}}$	17.2 (16.8)	18.0 [f] (17.5)
E_{tc}^{ex}	25.0 (24.4)	28.5 (28.0)
$E_{tc}^{\mathrm{e\text{-}h}}$	26.0 (25.5)	30.0

[a] Reference 14.
[b] Reference 19.
[c] Reference 31.
[d] Reference 20.
[e] Reference 9.
[f] Reference 24.
[g] Reference 22.

crossluminescence with the short-wavelength edge at ~8.5 eV. However, $E_{gc} > E_{ga} + E_{ea}$ and the Auger recombination of a conduction electron and a cation hole can lead to the formation of a secondary anion exciton in RbCl. The latter process can be responsible for our failure to detect the crossluminescence in the region of 7–9 eV under the irradiation of a RbCl crystal by a powerful 6 keV electron beam at 8 K.

Let us return now to the main phenomenon revealed at the investigation of MEE processes in RbCl:Tl and KCl:Tl crystals. If the energy of conduction electrons, formed due to the photoionization of anions or cations, is close to the energy of optical excitation of s^2 impurity ions (Tl^+), it can be transferred to Tl^+ centers with the excitation of typical A and B impurity emissions (${}^3P_1 \rightarrow {}^1S_0$ and ${}^3P_2 \rightarrow {}^1S_0$ electron transitions in a free Tl^+ ion).

We revealed the effect of impurity ion excitation by HPE's in a KCl:Tl crystal also. The quantitative parameters of this process are presented in Table I. Part of the data for KCl:Tl were presented at the International Conference on Luminescence, Prague 1996.[24] In RbCl:Tl there are narrow anion and cation valence bands and, hence, heavy cation and anion holes. Therefore electrons gain practically all the excess energy absorbed by a crystal ($h\nu - E_g$) above the threshold photon energy for ionization of cations or anions. According to Table I the values of $E_{ta}^{\mathrm{e\text{-}h}}$, E_{ta}^{ex}, E_{ta}^A, and E_{ta}^B in RbCl are only by 0.3–0.8 eV lower than those in KCl. On the other hand, the values $E_{tc}^{\mathrm{e\text{-}h}}$, E_{tc}^{ex}, E_{tc}^A, and E_{tc}^B in KCl exceed the similar values in RbCl by 3.5–4.2 eV reflecting the difference between the values of E_{gc} in these crystals.

Experimentally determined threshold energies for Tl^+ excitation up to the A state, $E_{ta}^A = 14$ eV and $E_{tc}^A = 22.5$ eV only slightly exceed the values ($E_{ga} + E_{\mathrm{abs}}^A$) and ($E_{gc} + E_{\mathrm{abs}}^A$). In RbCl:Tl, Tl^+ centers transform the absorbed energy into luminescence with a large Stokes shift, $E_{\mathrm{abs}}^A - E_{\mathrm{emis}}^A = 1.07$ eV and with the creation of more than 50 phonons. If the Tl^+ excitation to A state by HPE's, similar to the process of photon absorption, takes place in accordance with the Franck-Condon principle (quantum-mechanical case), a small difference between E_{ta}^A and ($E_{ga} + E_{\mathrm{abs}}^A$) should be explained as the result of low-energy losses of HPE's before their interaction with Tl^+ centers in RbCl:Tl (200 ppm). The theory of HPE interaction with impurity centers in wide-gap crystals is not elaborated. Therefore, it is difficult to estimate the probability of Tl^+ excitation by HPE's directly up to the minimum of adiabatic potential for A state. This minimum is located by ≈4.5 eV above the minimum for the ground state in RbCl:Tl. The above-mentioned conclusions are valid for the Tl^+ center in KCl:Tl also.

The functions of free ns^2 atom (Zn, Cd, Hg) excitation by electrons of various energies up to levels with different multiplicity are strongly different.[15,33] In the case of ${}^1S_0 \rightarrow {}^3P_1$ singlet-triplet transitions, the excitation function for atomic emission sharply reaches the maximum with an electron energy increasing above the threshold value. For ${}^1S_0 \rightarrow {}^1P_1$ transitions of free atoms the excitation function smoothly increases with the rise of the energy (velocity) of electrons and reaches a weakly manifested maximum at an energy exceeding the threshold value by 2–3 times. The sharp increase of probability for singlet-triplet transitions of a free atom in the threshold region is caused by effective electron exchange.[15]

A theoretical consideration of peculiarities of excitation functions for ns^2 impurity ions in wide-gap crystals is still absent. According to our experimental results described in the previous sections, the efficiency of A and B emissions of Tl^+ centers sharply increases when the photoelectron energy (relative to the bottom of CB) exceeds by 20% the threshold energy for the Tl^+ luminescence excitation by HPE's. The efficiency of Tl^+ phosphorescence excitation by HPE's, η_{ph} has sharp maxima at 15.2 and 16.6 eV in RbCl:Tl (see Fig. 2) and KCl:Tl (Ref. 24) crystals, respectively. The ${}^1S_0 \rightarrow {}^1P_1$ singlet-singlet transitions are responsible for the appearance of this recombination phosphorescence at 295 K. However, the decrease of η_{ph} in the region above the maximum occurs in a KCl crystal due to the effective creation of secondary anion excitons by 7.5–8.0 eV conduction electrons. The efficiency of SE formation at $h\nu > 16.6$ eV is significantly higher than that of Tl$^+$ center excitation by HPE's. In RbCl a similar decrease of η_{ph} can be attributed to the formation of cation excitations at 16–18 eV (see narrow reflection maxima in Fig. 3). Formation of secondary intrinsic EE's impedes the registration of excitation functions for the $^1P_1$ state of Tl$^+$ in a wide energy region of HPE's in KCl and RbCl crystals. Only further investigations of Tl$^+$ center excitation in crystals with extremely wide energy gap (e.g., KF) will allow us to compare the excitation functions for a $^1P_1$ state of an impurity ion in a crystal and the excitation function of singlet-singlet transitions in a free atom.

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