PHYSICAL REVIEW B VOLUME 52, NUMBER 14 1 OCTOBER 1995-II

Creation of stable Frenkel defects by vacuum uv radiation in KBr crystals under conditions of multiplication of electronic excitations

A. Lushchik, I. Kudrjavtseva, Ch. Lushchik, and E. Vasil'chenko
Institute of Physics, Estonian Academy of Sciences, Riia 142, EE2400 Tartu, Estonia

M. Kirm and I. Martinson
Department of Atomic Spectroscopy, Lund University, Sölvegatan 14, S-22362 Lund, Sweden

(Received 3 April 1995)

The spectrum of *F*-center creation has been measured for KBr:Tl by means of synchrotron radiation (12–24 eV). Analysis of the spectrum reveals the decay of cation excitons (19.7–20.3 eV) with the formation of a double amount of electron-hole pairs. The creation efficiency of a stable *F* center is especially high at 15–17 eV where the absorption of one photon leads to the formation both of an electron-hole pair and an exciton. In this case there are favorable conditions for stabilization of mobile radiation defects due to the association of interstitial halogen atoms, holes, and cation vacancies.

The creation of defects in wide-gap ionic crystals by radiation has been studied for many years,[1,2] but monochromatic radiation has been used in only a few experiments. Conventional absorption and electron paramagnetic resonance (EPR) methods are not sufficiently sensitive even for the investigation of Frenkel defect creation by vacuum ultraviolet (VUV) light in radiation-sensitive alkali halides. Therefore, highly sensitive luminescent and photoelectric methods must be used for the investigation of *F*-center (an electron localized near an anion vacancy) creation by VUV radiation. In the case of photostimulation of a crystal in the *F*-absorption band, recombinational luminescence or electron emission (for KBr, see Refs. 2 and 3) as well as infrared emission of *F* centers[4] has been detected in crystals which have undergone previous irradiation. The creation of anion vacancies (α centers) by VUV radiation can be detected by measuring the luminescence of the halogen ions surrounding an anion vacancy.[5] Although high-sensitivity methods have been used, the creation of *F* and α centers has been investigated in a narrow spectral region, of 6–9 eV only.[2-5] The application of synchrotron radiation (SR) has led to a significant broadening of the region where optical constants have been studied. This paper reports a measurement of the spectrum of *F*-center creation by SR (12–24 eV) in KBr:Tl. The aim of the present study was to investigate the processes of creation and stabilization of Frenkel defects under the conditions of multiplication of electronic excitations (MEE's). The process of MEE's, when one photon can create two or three electronic excitations, has been investigated for KBr earlier.[6-9]

It is well known that the main channel of radiation defect production in alkali halides is the decay of self-trapped excitons (STE's) with the formation of *F* centers and complementary *H* centers.[1,2] An *H* center is a Br_2^- two-halide molecule in one anion site.[10] About 5% of *F*-*H* pairs created by radiation at 4.2 K remain stable for many hours. The annealing of these *F*-*H* pairs occurs at 40–60 K. In this temperature range, *H* centers become mobile and partially recombine with *F* centers or form *H*-*H* associations which are stable up to 130 K. The optimal conditions of radiation defect stabilization at room temperatures, important for technical applications, are still unclear.

We have investigated the creation of *F* centers by SR of 12–24 eV for a KBr crystal doped by 300 ppm of Tl^+ ions. These ions served as sensitive luminescent probes for the detection of a small concentration of *F* centers. The excitation of KBr:Tl in the regions of *A*-, *B*-, and *C*-absorption bands (4.8, 5.7, and 5.9 eV, respectively) causes the appearance of Tl^+ luminescence (3–4 eV) with the quantum yield of about one at 295 K.[11] Irradiation of KBr by photons of $h\nu > E_g$ (E_g is the energy gap) leads to the formation of electrons and self-trapped holes (V_K centers). At 295 K, V_K centers are highly mobile and interact with Tl^+, thereby forming Tl^{2+} centers. The recombination of an electron with Tl^{2+} takes place via an excited state of Tl^+ and leads to the appearance of luminescence (3–4 eV) of Tl^+ centers. Figure 1 presents a spectrum of the stimulation of Tl^+ luminescence (by an equal number of photons in the interval 1.5–2.5 eV) for a KBr:Tl crystal previously irradiated by 7.8-eV photons which created electron-hole (*e*-*h*) pairs. Figure 1 also shows the absorption band with its maximum at 1.97 eV, connected with *F* centers. Mainly *F* centers are formed in the irradiated KBr:Tl crystal. A small amount of other color centers (*F* perturbed by Tl^+ impurity ions[12]) is responsible for the absorption band with maximum at about 1.8 eV. In this paper we shall consider the formation of *F* centers only.

Experiments were partly carried out at beam line 52 in MAX-Laboratory, Lund (550-MeV storage ring). The experimental setup has been described in Refs. 7 and 13. The crystal was irradiated by a prescribed number of photons at each of several energies ($\approx 10^{15}$ cm^{-2}). For KBr at 295 K, the absorption constant is about 10^5 cm^{-1} in the region of 12–24 eV. The quantum yield of a stable *F*-center creation by 9-eV photons is about 10^{-2} for KBr and KCl at 295 K.[1,3] So, according to our estimates, the

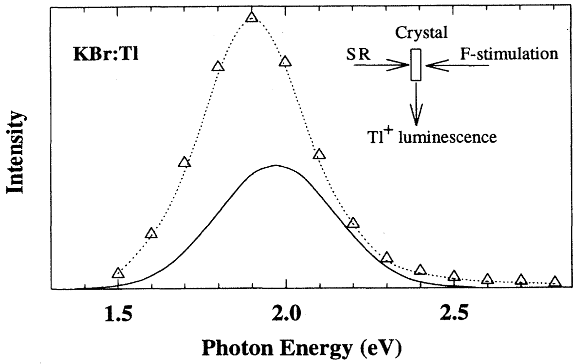

FIG. 1. Stimulation spectrum of Tl$^+$ emission in a KBr:Tl crystal previously irradiated by photons of 7.8 eV (△). The absorption spectrum of single *F* centers in KBr (solid line). All spectra were measured at 295 K. The inset shows the geometry for measuring the spectrum of *F*-center creation by means of luminescent method.

number of *F* centers created by SR in KBr:Tl is about 10^{18} cm^{-3}. The previously irradiated crystal was stimulated through a double monochromator by 2.00±0.03-eV photons, causing the ionization of *F* centers. A second monochromator was used to detect the 4-eV luminescence of Tl$^+$ centers. The light sum of this Tl$^+$ luminescence stimulated in the *F*-absorption band was taken as a measure of *F* centers created by SR. Before measuring the next point in the creation spectrum, photodestruction of the remaining *F* centers was carried out by means of intensive *F* stimulation of a crystal.

Figure 2 presents the reflection and the *F*-center creation spectrum of the KBr:Tl sample at 295 K. The reflection maxima practically coincide with the maxima of the absorption bands for epitaxial films of KBr.[3,16] The reflection maxima between 19.5 and 24 eV are connected with the formation of cation electronic excitations.[7,8,14,15]

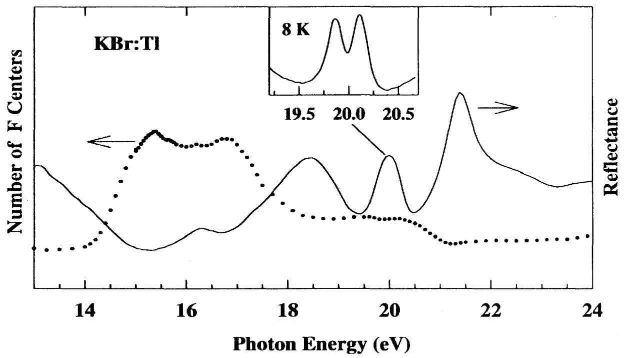

FIG. 2. Spectrum of *F*-center creation (●) by SR measured for KBr:Tl at 295 K using luminescent method. The optical slit width of 3.3 Å was used on the crystal irradiation. The reflection spectrum for the (100) plane of a freshly cleaved KBr:Tl crystal at 295 K (solid line). The inset shows a fragment of the reflection spectrum (optical slit width of 0.8 Å) for KBr at 8 K.

The efficiency of *F*-center creation, η_F, is low at 13–14 eV, starts to increase at 14.2 eV, and reaches maxima at 15.4 and 16.8 eV. Earlier we studied the process of secondary exciton formation by hot photoelectrons in KBr at 8 K. Efficiency maxima of this process at 15.8 and 16.8 eV have been detected thereby.[7] The maxima in the η_F spectrum at 15.4 and 16.8 eV should be ascribed to the formation of secondary triplet Γ excitons by hot photoelectrons. It is necessary to mention that the increase of η_F at 14.2–15.4 eV is slower than the efficiency increase of secondary exciton formation in KBr at 8 K (see Ref. 7). The range 14.2–15.4 eV, connected with the formation of secondary excitons by hot photoelectrons at 295 K, can be considered as an analog of the Urbach tail of exciton absorption (6.1–6.6 eV), which has been investigated in detail.[16] In alkali halides it is caused by the creation of excitons in the self-trapped state.[1] For KBr at 295 K, a minimum energy of STE formation by a photon equals $E_e = 6.1$ eV,[16] while the value of E_g equals 7.4 eV.[3] The spectrum of *F*-center creation in KBr:Tl yields the value of the threshold energy for the formation of secondary STE's, $E_{\text{th}}^0 = 14.3 \pm 0.2$ eV. The energy excess $E_{\text{th}}^0 - (E_g + E_e) = 0.8$ eV is gained by a heavy hole formed along with a light conduction electron on the absorption of a 14.3-eV photon.

Figure 2 shows that the value of η_F decreases sharply at 17–18 eV and stays constant at 18–20.5 eV, being now twice as high as at 13–14 eV, where one photon creates one *e-h* pair. In the region of 17–19 eV, hot photoelectrons create secondary *e-h* pairs, causing the doubling of η_F. The SR of 19.5–20.5 eV creates in KBr cation excitons[14,15] with a resolved spin-orbit splitting in the reflection spectrum at 8 K (see inset in Fig. 2). The value of η_F at the decay of cation excitons is practically the same as in the region where one photon forms two *e-h* pairs. Our data and those concerning the quantum yield of photoelectron emission in KBr (Ref. 8) show that the decay of one $3p^5 4s$ cation exciton leads to the formation of two *e-h* pairs with similar characteristics, as a result of the law of conservation of the quasi-impulse. In this case the energy excess given to each of the two photoelectrons at the moment of creation equals 1.8 eV only (relative to the bottom of the conduction band). Most of these photoelectrons lose more than half of their energy on their way to the surface as a result of interactions with phonons and thus cannot leave the crystal [the electron affinity in KBr is $\chi = 0.9$ eV (Ref. 8)]. Figure 2 shows that the value of η_F begins to decrease at $h\nu > 20.5$ eV, i.e., in the same region where a typical shoulder in the reflection (absorption) spectrum has been observed.[7,14] We interpret this decrease as a manifestation of the photoionization of the K$^+$ ion, when an electron appears near the bottom of the conduction band (with an energy less than χ) and a hole appears in the $3p^6$ shell of K$^+$. The nonradiative Auger recombination of a hole in the $3p^6$ shell of K$^+$ with an electron in the $3p^6$ shell of Br$^-$ leads to a transfer of the energy release (11–12 eV) to a valence electron and the subsequent formation of a second hole in the valence band and a second conduction electron with the energy of ≈4.5 eV. The latter electron

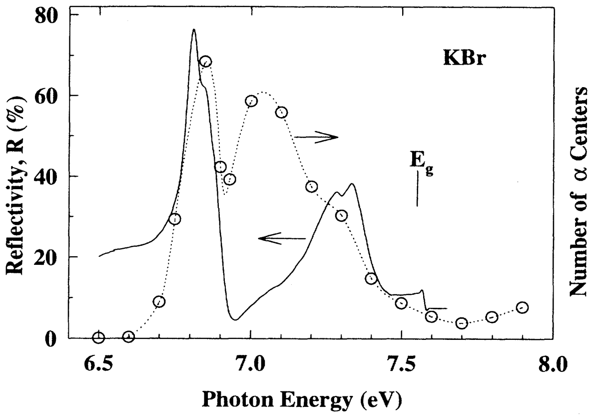

FIG. 3. Spectrum of α-center creation by VUV radiation (○) and the reflection spectrum (solid line) for a KBr crystal at 4.2 K. An optical slit width of 17 Å was used on the crystal irradiation.

has a high probability to leave the crystal, resulting an effective electron emission. This leads to a decrease in the recombination of electrons with self-trapped holes and in the F-center creation efficiency η_F. Our data indicate that the threshold energy of K^+ photoionization is $E_{th} = 20.5 \pm 0.2$ eV.

The creation spectrum of stable F centers (and complementary H centers) in the region of 15–17 eV is of special interest. The absorption of a photon here leads to the formation of one e-h pair and one exciton. In this case there are favorable conditions for stabilizing the radiational defects, mobile at 295 K. Our data show that the multistage annealing of F centers in irradiated KBr and KBr:Tl occurs at 320–440 K. The main stage of F-center annealing takes place at 380 K, i.e., in the same temperature range as the thermal dissociation of trihalide Br_3^- molecules, which are situated at two anion and one cation sites and oriented along $\langle 100 \rangle$ directions (see Refs. 17 and 18). The formation of stable Br_3^- by radiation at 295 K requires the association of three mobile defects, an H center, a hole, and a cation vacancy. The irradiation of KBr by 15–17-eV photons is favorable for simultaneous creation of holes and H and F centers. The mechanism of radiation creation of cation vacancies, which are undoubtedly components of stable Br_3^- centers, has to be elucidated.

In principle, a cation vacancy and an interstitial metal ion can be formed on the nonradiative decay of cation excitons.[18] However, our experimental data for KBr demonstrate that a cation exciton decays with the formation of two e-h pairs. At the same time, stable F and Br_3^- centers can be effectively created by 15–17-eV photons which form e-h pairs and anion excitons, but not cation excitons. In this case cation defects can be created either by the recombination of electrons and holes[2] or through the association of H centers with holes.[18]

Figure 3 shows a spectrum of an anion vacancy creation by VUV radiation of 6.5–8 eV from a discharge source in KBr at 4.2 K. We studied zone-refined KBr crystals for which the concentration of Na^+ and I^- impurity ions is about 3 ppm, Cl^- about 30 ppm, and those of OH^- and Sr^{2+}, 0.01 ppm. The crystal was irradiated at 4.2 K by a prescribed number of photons ($\approx 10^{13}$ cm^{-2}) for several different energies. The intensity of 6.15-eV-photon-stimulated (in the maximum of the α-absorption band) α luminescence of 2.6 eV was taken as a measure of the number of α centers in KBr. The spectrum was corrected for the reflection of VUV radiation by the crystal. After measuring every point in the spectrum, the crystal was heated to 295 K. On heating of the crystal to 30 K, an annealing of 75% of α centers occurs as a result of the recombination of anion vacancies with mobile I centers. The annealing of the remaining α centers takes place between 40 and 100 K.

A comparison of the spectrum of α-I pair creation (I is an interstitial halogen ion) with that of intrinsic absorption (reflection) of KBr (interpreted in detail by many authors; see Ref. 1) allows us to conclude that the efficiency of α-I pair creation is especially high at the generation of triplet and singlet Γ excitons by 6.75–7.5-eV photons. In the case of photon energies exceeding $E_g = 7.55$ eV, this efficiency is by a factor of 10 lower. Tunnel recharging of these F and H centers at 4.2 K leads to the formation of long-lived (stable) α-I pairs.[19]

Decay of excitons at 295 K leads to the formation of F and H centers with interdefect separation r_{FH} so large that the subsequent tunnel recharging of these defects is precluded. However, the recombination of an electron with a self-trapped hole produces an F-H pair with a smaller value of r_{FH}. As a result, F-H pairs are partially converted into α-I pairs by means of tunneling recharging. According to calculations of Rowell and Sangster,[20] the formation energy (under thermal equilibrium conditions) for cation Frenkel defects (3.27 eV) is lower than that of anion Frenkel defects (4.52 eV) in KBr. From this we conclude that the nonradiative recombination of interstitial halogen ions with anion vacancies leads not only to heat release, but also to the creation of cation vacancies and interstitial metal ions. At high temperatures ($T > 170$ K for a KBr crystal), the mutual separation of such cation Frenkel defects is possible. The association of mobile H centers and self-trapped holes with cation vacancies leads to the formation of trihalide Br_3^- molecules, situated at two anion and one cation sites and stable up to 370–400 K. Another kind of Br_3^-, stable up to 350–370 K, is formed as a result of the association of an H center with a hole.[18]

Finally, we conclude that the absorption of one photon with the energy of 15–17 eV leads to the formation a primary electron-hole pair and a secondary exciton. In this case there are favorable conditions for stabilization of radiation defects mobile at 295 K. An analogous but more complicated process of defect stabilization takes place in photographic materials. In silver halides a stable center of the latent image is formed if the energy of absorbed photon is sufficient to produce three e-h pairs.[21]

The authors are grateful to Dr. E. Feldbach and Dr. R. Kink for valuable discussions. This work has been partly supported by the Estonian Science Foundation, the Swedish Natural Science Research Council (NFR), the Royal Swedish Academy of Sciences, the Crafoord Foundation, the Carl Trygger Foundation, and the Magn. Bergvall Foundation.

[1] K. S. Song and R. T. Williams, *Self-Trapped Excitons* (Springer-Verlag, Berlin, 1993), and references therein.

[2] Ch. B. Lushchik, I. K. Vitol, and M. A. Elango, Usp. Fiz. Nauk **122**, 223 (1977) [Sov. Phys. Usp. **20**, 489 (1977)], and references therein.

[3] Kh. R.-V. Iygi *et al.*, Fiz. Tverd. Tela **14**, 117 (1972) [Sov. Phys. Solid State **14**, 95 (1972)].

[4] B. R. Sever, N. Kristianpoller, and F. C. Brown, Phys. Rev. B **34**, 1257 (1986).

[5] E. A. Vasil'chenko *et al.*, Fiz. Tverd. Tela **23**, 481 (1981) [Sov. Phys. Solid State **23**, 271 (1981)].

[6] Yu. M. Aleksandrov *et al.*, Fiz. Tverd. Tela **24**, 740 (1982) [Sov. Phys. Solid State **24**, 418 (1982)].

[7] A. Lushchik, E. Feldbach, Ch. Lushchik, M. Kirm, and I. Martinson, Phys. Rev. B **50**, 6500 (1994).

[8] A. Ejiri, A. Hatano, and K. Nakagawa, J. Phys. Soc. Jpn. **63**, 314 (1994).

[9] E. R. Ilmas, G. G. Liidja, and Ch. B. Lushchik, Opt. Spektrosk. **18**, 631 (1965) [Opt. Spectrosc. (USSR) **18**, 359 (1965)].

[10] W. Känzig and T. O. Woodruff, Phys. Rev. **109**, 220 (1958).

[11] P. W. M. Jacobs, J. Phys. Chem. Solids **52**, 35 (1991).

[12] E. Goovaerts *et al.*, Phys. Rev. B **24**, 29 (1981).

[13] R. Kink *et al.*, Phys. Scr. **43**, 517 (1991).

[14] D. Blechschmidt *et al.*, Phys. Status Solidi B **44**, 787 (1971).

[15] T. G. Sprussel, M. Skibowski, and V. Saile, Solid State Commun. **32**, 1091 (1979).

[16] T. Tomiki, T. Miyata, and H. Tsukamoto, Z. Naturforsch. A **29**, 145 (1974).

[17] A. Baimakhanov, Kh. R.-V. Iygi, and Ch. B. Lushchik, Fiz. Tverd. Tela **28**, 684 (1986) [Sov. Phys. Solid State **28**, 381 (1986)].

[18] Ch. Lushchik *et al.*, Semicond. Insul. **5**, 133 (1980).

[19] A. Ch. Lushchik and A. G. Frorip, Phys. Status Solidi B **161**, 525 (1990).

[20] D. K. Rowell and M. J. L. Sangster, J. Phys. C **14**, 2909 (1981).

[21] V. M. Belous, E. R. Ilmas, and N. S. Rooze, Fiz. Tverd. Tela **11**, 606 (1969) [Sov. Phys. Solid State **11**, 488 (1969)].