

Exciton self-trapping into diatomic and triatomic molecular complexes in xenon cryocrystals

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The recent study of molecular trapped centers in Xe cryocrystals was extended on triatomic self-trapped excitons. Time- and spectrally-resolved molecular luminescence was measured in the temperature range 5–60 K. The processes of intrinsic exciton self-trapping into diatomic and triatomic molecular complexes and extrinsic exciton trapping at lattice imperfections were separated by selective photoexcitation of Xe cryocrystals by synchrotron radiation. The temperature dependencies of triplet lifetimes of molecular exciton subbands were measured for the first time.

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1. Introduction

Rare-gas cryocrystals are attractive objects for investigation of electronic excitation trapping processes in condensed matter. Because of strong coupling with phonons free excitons (FE) in rare-gas cryocrystals are localized into quasi-atomic and quasi-excimer (excited dimer) self-trapped excitonic states (STE). Radiative decay of quasi-excimer trapped excitons produces the most prominent feature in a vacuum-ultraviolet (VUV) luminescence from solid Ar, Kr and Xe – the so-called *M*-band (molecular luminescence band) which is formed by $^1,3\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ transitions in molecular dimer R_2^* imbedded in the host lattice (*R* stands for a rare-gas atom) [1]. The hole part of the STE is self-trapped between two neighboring rare-gas atoms in the diatomic bonding configuration, and the excited electron is bound to it primarily by the Coulomb interaction [2]. The internal structure of the *M*-band, which indicates the peculiarities of crystal lattice structure, has been studied recently [3]. Translational motion of a molecular-STE along the

atomic chain by continuous redistribution of the hole part of exciton among atoms inevitably passes a symmetric triatomic configuration, which is presumed to be a metastable [4]. However, in solid Xe at elevated temperature ($T > 50$ K) in addition to M_1 and M_2 molecular luminescence subbands of *M*-band the third molecular band at 7.6 eV (M_3 -band) appears in the emission spectrum of molecular self-trapped excitons. It was suggested that the M_3 -band is attributed to radiative decay of excitons self-trapped into triatomic linear molecular complexes [5], whose electronic and geometric structure was studied recently [6].

Such a variety of trapping channels for excitons makes solid Xe a suitable media for modeling the processes of self-trapping of electronic excitations [2]. The paper reports the results of the analysis of the time- and spectrally-resolved luminescence from excited diatomic and triatomic intrinsic molecular complexes in Xe cryocrystals following primary selective excitation by synchrotron radiation in the temperature range 5–60 K.

2. Experiment

The photoluminescence experiments were carried out at the SUPERLUMI experimental station at HASYLAB, DESY, Hamburg. The selective photon excitation was performed with $\Delta\lambda = 0.2$ nm. The low-resolution spectral and time-resolved analysis of the molecular luminescence was performed with a high-flux VUV-monochromator equipped with a multisphere plate detector. The convolution of the temporal behavior of the excitation synchrotron pulse, the response of the detector and of the electronics used was about 430 ps. High-resolution spectra were measured with $\Delta\lambda = 0.1$ nm by a 1-m near-normal incidence VUV-monochromator equipped with a position-sensitive detector. The cathodoluminescence measurements were performed at the molecular spectroscopy laboratory of Verkin Institute, Kharkov. The electron beam excitation was performed by electrons of energy 1 keV, insufficient to form defects by elastic collisions. The luminescence analysis with $\Delta\lambda = 0.2$ nm was carried out with a 1-m near-normal incidence monochromator equipped with a solar-blind photomultiplier.

The crucial part of the luminescence experiments with rare-gas solids is the sample preparation technique. There are two most common used methods of Xe sample preparation from vapor phase: (i) isothermal growth at $T = 118$ K with growing rate of about $1 \mu\text{m}/\text{min}$, and (ii) growing of the sample under isobaric ($P \approx 1000$ Pa) conditions with the constant cooling in the temperature range 125–110 K. The isothermal growth is rather slow, but it provides the preparation of the samples with the best crystal quality [7]. The isobaric growth is much faster and it allows to vary the quality of the crystals by changing the cooling rate from 0.01 K/s («slow» isobaric growth with growing rate about $10 \mu\text{m}/\text{min}$) to 0.5 K/s («fast» isobaric growth with growing rate about $50 \mu\text{m}/\text{min}$). In the present study we used the fast isobaric method of sample preparation. The samples were grown in situ on copper substrate from a high purity (99.999%) room temperature vapor phase in special closed cells [8]. The thickness of the samples was ≈ 0.5 mm.

3. Results and discussion

The VUV-luminescence spectra of solid Xe at temperatures below and above the threshold of M_3 -band appearing are shown at Fig. 1. The broad Stokes shifted STE-emission band (M -band) contains contributions of radiative decay of quasi-excimer centers of two types [3]. Depending on the structure of surrounding lattice the molecular STE centers emit dif-

ferent subbands of molecular luminescence band – high-energy subband M_2 is emitted by STE quasi-excimer in perfect lattice, whereas the low-energy subband M_1 is emitted by molecular excitons, which are trapped at lattice imperfections. The analysis of mutual behavior of subbands at various treatments of the samples under selective photoexcitation allows us to elucidate the complicated picture of branched relaxation of electronic excitations in rare-gas cryocrystals [9].

The high-resolution spectra of Xe cryocrystals in the FE-emission range are shown at Fig. 1,c. The narrow line at $E_{FE} = 8.36$ eV (FE-line) is formed by radiative decay of free excitons from the bottom of the lowest $\Gamma(3/2)$, $n = 1$ excitonic band. The energetic position of the maximum of FE-line exhibits the temperature shift because of thermal expansion of the lattice [10]. In addition, in the spectra of Xe cryocrystals, grown by fast isobaric method, two luminescence features appear: the narrow band at 8.15 eV in whole temperature range and the weak asymmetric band at 8.23 eV at high temperature (Fig. 1,c). The 8.15 eV band (E_2 -band) has been reported earlier in cathodoluminescence [8,10] and in laser- and x-ray-excited luminescence spectra [11]. The intensity of E_2 -band grows when the crystal quality of the sample decreases [8]. The asymmetric band at 8.23 eV is attributed to luminescence from «hot» states of molecular self-trapped excitons in solid Xe [11,12]. Both E_2 -band and 8.23 eV-band were not visible in the spectrum of the best sample of solid Xe [7] prepared by isothermal growth. On the same time in laser- and x-ray-excited luminescence there were no FE-line. One can suggest that formation of both 8.15 eV and 8.23 eV emitting centers is stimulated by crystal lattice imperfections.

Above $T = 50$ K the third wide molecular-like band M_3 centered at 7.63 eV with FWHM 0.36 eV appears in addition to M_1 and M_2 molecular luminescence bands (Fig. 1,b). Up to now there is no final conclusion about the nature of this high-temperature molecular band in solid Xe. At the very beginning of the study of excitons in rare-gas solids it was suggested that the M_3 -band is emitted by real STE in the perfect lattice, whereas the band M corresponds to excitons localized at lattice defects [13,14]. This hypothesis contradicts to recent studies of exciton self-trapping into molecular states in rare-gas cryocrystals [3,5,7,9,12] and excludes the exciton self trapping in solid Kr and Ar, where there is no luminescence band similar to solid Xe M_3 -band. There were several attempts to associate the M_3 -band with the forbidden transition $^1\Sigma_g^+ \rightarrow ^1\Sigma_g^+$ [15], with emission from high-energy molecular states $^{13}\Pi_g$ [16] and with ra-

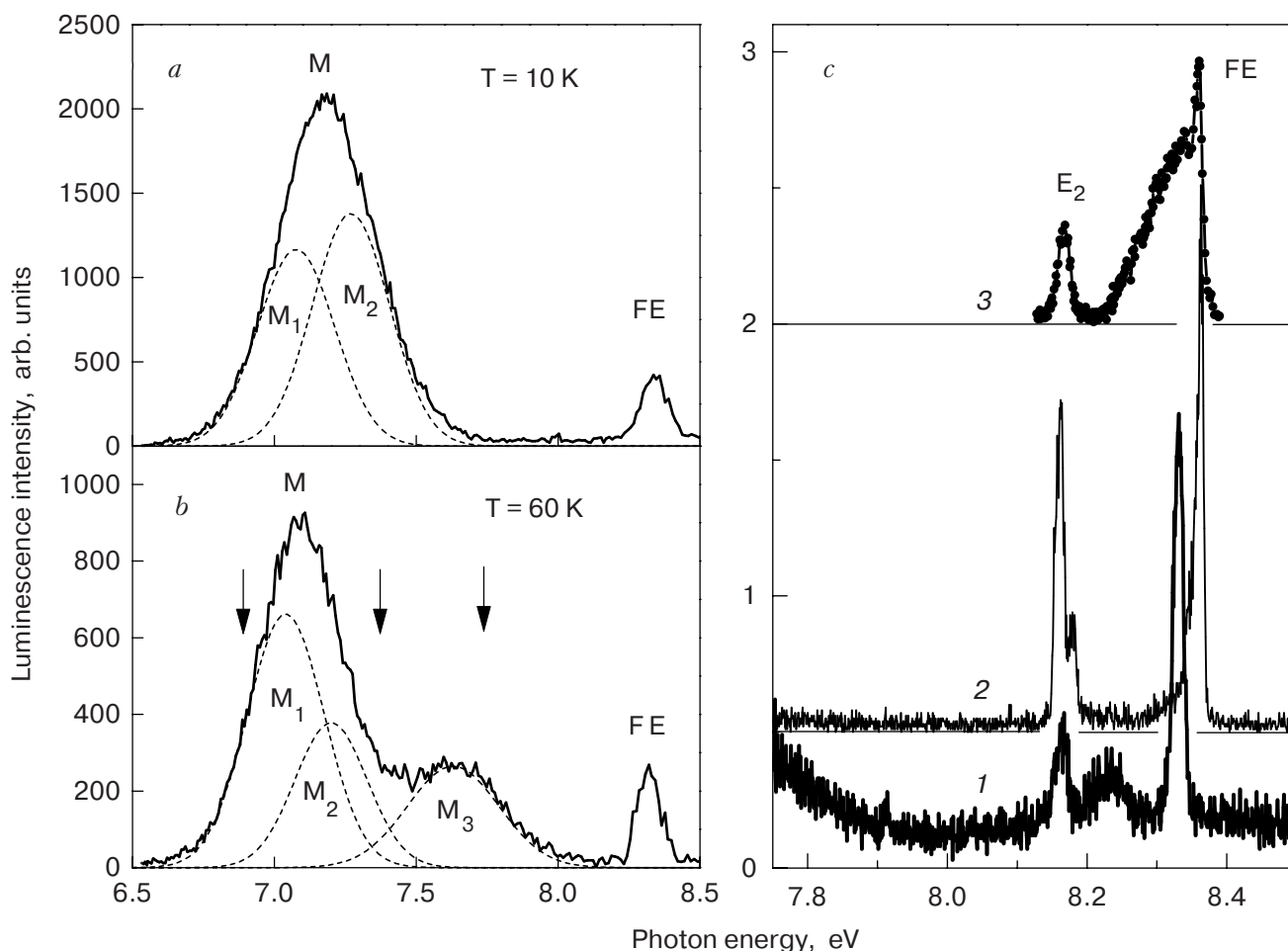


Fig. 1. Luminescence spectra of Xe cryocrystals under selective photoexcitation with $h\nu = 8.86$ eV (a) and (b). Photo-luminescence (curves 1 and 2) and cathodoluminescence (curve 3) spectra of solid Xe at $T = 10$ K (curves 2 and 3) and $T = 60$ K (curve 1) (c).

diative decay of the $n = 2$ STE [17]. The alternative explanation of the origin of the M_3 -band was proposed by Ratner et al. [5]. Basing on the concentration dependence of the M_3 -band intensity in the various systems Xe/Rg (Rg denotes Kr, Ar, Ne) and comparison of this dependence with the similar dependence of the M -band, it was suggested that M_3 -band is emitted by linear triatomic excited molecular centers self-trapped in a perfect lattice [5]. Each of the two resonant bindings in the linear triatomic complex Xe_3^* is weaker compared to a single binding in the quasi-excimer Xe_2^* and a correspondent elongation of the binding in the Xe_3^* results in a blue shift of the M_3 -band compared to that in the diatomic molecule [5]. Such triatomic linear complexes are inevitably forming during translation motion of molecular excitons in perfect lattice [4]. Recent accurate calculations of linear Xe_3^+ [18] and Xe_2^+ [19] molecular ions confirm this trend. In the linear ion Xe_3^+ the charge e is distributed over the three atoms like 0.239–0.523–0.239 (e) and the length of the bonds is

3.274 Å [18], whereas in the Xe_2^+ -ion the bond length is 3.11 Å [19]. Assuming the similarity of the hole part of STE with correspondent molecular ions [2] we suppose the similar elongation of the bond in the Xe_3^* in comparison with Xe_2^* . In addition to linear symmetric configuration of Xe_3^+ cation the only stable asymmetric triatomic configuration was found – triangular structure with the positive charge localized on two atoms with the third, almost neutral atom, attached in an equilateral position [18]. The length of the bond between charged atoms in this case is 3.12 Å [18] and the emission from such triangular centers in solid Xe, if ever occurs, may contribute to M_1 -subband. This is the possible reason why the M_3 -band has no «defect» subband.

Excitation spectra of luminescence bands from various trapped centers reveal peculiarities of different channels and branching between them in relaxation of electronic excitations [1,3,9]. Strong overlapping of molecular components of the luminescence from solid Xe above $T = 50$ K gives no way to record the excita-

tion spectra of subbands by scanning the photon excitation energy by primary monochromator at fixed detection wavelength of secondary monochromator. To restore the excitation spectra of M_1 , M_2 , and M_3 subbands we used the method of decomposition of the sequence of luminescence spectra, measured at different excitation energies [3]. Figure 2,*a* shows the restored excitation spectra at $T = 60$ K. The similarity of excitation spectra of M_2 and M_3 bands underlines their common intrinsic nature of emitting trapping centers – self-trapped excitons, whereas antibate behavior of excitation spectrum of «defect» M_1 subband reflects the competition of the processes of extrinsic exciton trapping at lattice defects and the exciton self-trapping. One of the possible processes which stimulate the high intensity of the excitation spectrum of the M_1 subband below the bottom of the lowest excitonic band is the process of trapped center creation as a result of formation of nucleation states responsible for electronic excitation localization due to thermal lattice disorder in the ground state [21]. Formation of such centers intensifies near the lattice defects and direct photoabsorption by such centers [22] results in M_1 -band emission.

Both the triplet $^3\Sigma_u^+$ and singlet $^1\Sigma_u^+$ states of the STE contribute to M -band and decay curve of molecular luminescence yields a slow decay component and a fast one. The fast decay component is independent of temperature [1]. The slow decay component exhibits pronounced temperature dependence because of phonon mixing of $^3\Sigma_u^+$ substates [20]. The lifetime obtained asymptotically at low temperature is ascribed to the totally forbidden A_u state. With increasing temperature, it can also be depleted by phonon transitions to the allowed $B_{3u,2u}$ state, which then radiates. Coexistence in solid Xe of two types (intrinsic and extrinsic) of excimer-like emitting centers implies different efficiency of the process of phonon mixing of $^3\Sigma_u^+$ substates depending on crystal lattice surroundings of these centers. It should result in differences in temperature dependence of triplet lifetimes of M_1 and M_2 subbands.

For the first time we have measured the decays of M_1 and M_2 subbands (Fig. 2,*b*) at photon energies, denoted at Fig. 1,*b* by arrows, under excitation by photons with energies $h\nu_1 = E_{FE}$ and $h\nu_2 = 8.86$ eV (denoted at Fig. 2,*a*). In the temperature range 10–50 K the temperature dependence of triplet life-

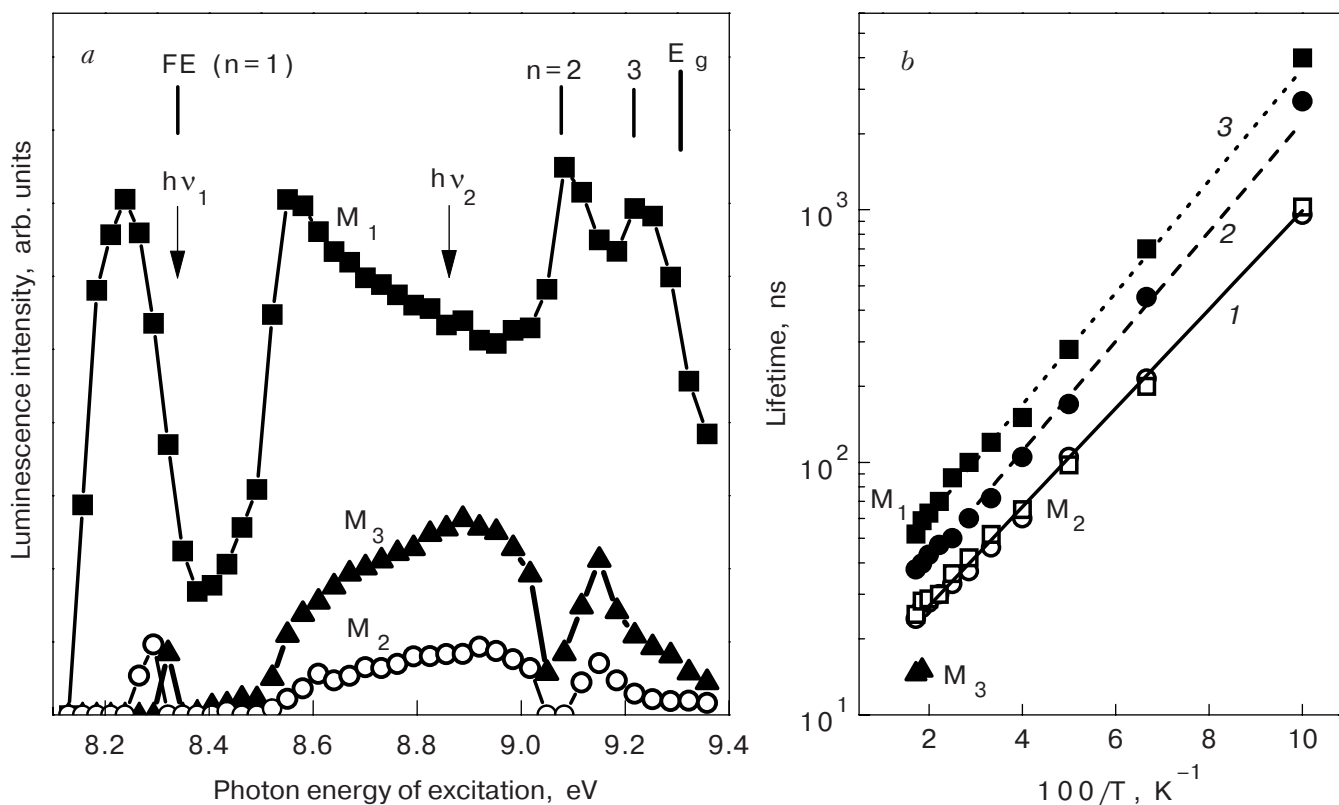


Fig. 2. Excitation spectra of molecular subbands of solid Xe at $T = 60$ K (*a*). Temperature dependence of the triplet lifetime of molecular subbands of solid Xe (luminescence energy; excitation energy), detected at photon excitation energies, denoted at Fig. 1,*b* by arrows under selective photoexcitation with energies $h\nu_1 = E_{FE}$ and $h\nu_2 = 8.86$ eV, arrows of Fig. 2,*a* (*b*). $M_1(6.89$ eV; $h\nu_1$) (■); $M_1(6.89$ eV; $h\nu_2$) (●); $M_2(7.38$ eV; $h\nu_1$) (□); $M_2(7.38$ eV; $h\nu_2$) (○); $M_3(7.74$ eV; $h\nu_2$) (▲).

time may be well approximated by single exponent $\tau(T) = C \exp(D/T)$, where C and D are fitting constants. Both temperature dependencies for M_2 subband may be approximated by the same exponent with $C_1 = 11$ ns and $D_1 = 45$ K (Fig. 2, *b*, curve 1) and phonon mixing of the triplet substates in the self-trapped excimer-like excitons independent of photon excitation energy. On the contrary, the decay of «defect» subband M_1 yields different temperature dependencies at different excitation energies: at excitation by photons with energies $E = 8.86$ eV, the fitting constants are $C_2 = 15$ ns and $D_2 = 50$ K (Fig. 2, *b*, curve 2), whereas at excitation by photons with energies equal to energy of the lowest $\Gamma(3/2)$, $n = 1$ excitons, $E = E_{FE}$, the fitting constants are $C_3 = 22$ ns and $D_3 = 51$ K (Fig. 2, *b*, curve 3). The acceleration of decay of M_1 subband with increasing excitation energy is in line with our recent analysis of relaxation of electronic excitations below E_g . As excitation energy nears E_g , the trapping cross section of excitons by lattice defects, which results in M_1 subband emission, grows proportionally to $\rho^{2/3}$ (ρ is the exciton-state radius) [9]. The lifetime of the M_3 -band was measured only in the temperature range 50–60 K since the high-vacuum requirements of the equipment working with synchrotron radiation do not allow to increase the temperature of Xe sample above 60 K. It yields $\tau(M_3) = 15$ ns at both excitation energies.

Thus, the analysis of luminescence of molecular centers of Xe cryocrystals under selective photoexcitation within excitonic energy range in temperature range 5–60 K demonstrates the similar intrinsic nature of M_2 and M_3 bands. They are emitted by diatomic and triatomic excitons self-trapped in perfect lattice. The extrinsic exciton trapping at lattice imperfections is competitive channel of exciton relaxation. It results in M_1 subband emission.

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1. N. Schwentner, E.E. Koch, and J. Jortner, *Electronic Excitations in Condensed Rare Gases, Springer Tracts in Modern Physics*, Vol. 107, Springer-Verlag, Berlin (1985).
2. K.S. Song and R.T. Williams, *Self-Trapped Excitons, Springer Series in Solid-State Sciences*, Vol. 105, Springer-Verlag, Berlin (1993).
3. A.N. Ogurtsov and E.V. Savchenko, *J. Low Temp. Phys.* **122**, 233 (2001).
4. A.M. Ratner, *Phys. Lett.* **A298**, 422 (2002).
5. A.M. Ratner, I.Ya. Fugol, A.G. Belov, and Yu.L. Steshenko, *Phys. Lett.* **A137**, 403 (1989).
6. J.A. Gascon, R.W. Hall, C. Ludewigt, H. Haberland, *J. Chem. Phys.* **117**, 8391 (2002).
7. D. Varding, I. Reimand, and G. Zimmerer, *Phys. Status Solidi* **B185**, 301 (1994).
8. I.Ya. Fugol, A.N. Ogurtsov, O.N. Grigorashchenko, and E.V. Savchenko, *Fiz. Nizk. Temp.* **18**, 44 (1992) [*Low Temp. Phys.* **18**, 27 (1992)].
9. A.N. Ogurtsov, A.M. Ratner, E.V. Savchenko, V. Kisand, and S. Vielhauer, *J. Phys.: Condens. Matter* **12**, 2769 (2000).
10. I.Ya. Fugol, O.N. Grigorashchenko, E.V. Savchenko, *Phys. Status Solidi* **B111**, 397 (1982).
11. M. Selg, M. Kink, R. Kink, J. Maksimov, and I. Martinson, *Surf. Rev. Lett.* **9**, 609 (2002).
12. A.N. Ogurtsov, E.V. Savchenko, S. Vielhauer, and G. Zimmerer, *HASYLAB Annu. Rep. 2001*, DESY, Hamburg (2002), p.279.
13. O. Cheshnovsky, A. Gedanken, B. Raz, and J. Jortner, *Solid State Commun.* **13**, 639 (1973).
14. R. Kink, A. Lohmus, and M. Selg, *Phys. Status Solidi* **B107**, 479 (1981).
15. R. Heumuller and M. Creuzburg, *Opt. Commun.* **26**, 363 (1978).
16. I.Ya. Fugol, *Adv. Phys.* **37**, 1 (1988).
17. K.M. Monahan and V. Rehn, *Nucl. Instrum. Methods Phys. Res.* **152**, 255 (1978).
18. R. Kalus and D. Hrivnak, *Chem. Phys.* **278**, 21 (2002).
19. I. Paidarova and F.X. Gadea, *Chem. Phys.* **274**, 1 (2001).
20. R. Kink, A. Lohmus, M. Selg, and T. Soovik, *Phys. Status Solidi* **B84**, K61 (1977).
21. J.L. Gavartin and A.L. Shluger, *Phys. Rev.* **B64**, 245111 (2002).
22. A.N. Ogurtsov, E.V. Savchenko, E. Gminder, S. Vielhauer, and G. Zimmerer, *Surf. Rev. Lett.* **9**, 45 (2002).