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Second- and Third-order Raman Scattering in Bulk and Glass-embedded Nanometric $CdS_{1-x}Se_x$ Crystals

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Second- and third-order Raman spectra of bulk and nanometric $CdS_{1-x}Se_x$ crystals were measured. At off-resonance excitation conditions the second-order Raman spectra of bulk $CdS_{1-x}Se_x$ exhibit anharmonic coupling of optical phonons and two-phonon states with the participation of acoustic phonons. Resonant Raman spectra of $CdS_{1-x}Se_x$ single crystals with a strong enhancement of multiple LO phonon bands show the evidence for the strong electron-phonon coupling in bulk $CdS_{1-x}Se_x$ crystals. From the ratio of intensities of multiple and single LO phonon bands in the resonance Raman spectra of the glass-embedded $CdS_{1-}Se_x$ nanocrystals one may conclude that the electron-phonon coupling in the nanocrystals is much smaller than in the corresponding bulk materials.

Keywords: Raman scattering, Nanocrystals, Electron-phonon coupling.

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1. INTRODUCTION

Compositional dependences of the first-order Raman spectra of ternary $CdS_{1-x}Se_x$ single crystals have been studied quite extensively, exhibiting two-mode behaviour (See e. g. [1] and references therein). Under resonance Raman excitation conditions, due to the Fröhlich coupling between free excitons and long-wavelength optical phonons [2], a series of LO phonon overtones was observed – up to nine for CdS [3]. Meanwhile, higher-order Raman scattering in mixed $CdS_{1-x}Se_x$ single crystals is studied much less extensively [4]. In particular, multiphonon Raman spectra of semiconductors are strongly determined by electron-phonon coupling [5, 6].

$CdS_{1-x}Se_x$ nanocrystals are grown in a glass matrix by solid-state precipitation from a supersaturated solution [7, 8] or produced by colloidal synthesis [9]. For these materials, resonance Raman spectroscopy is an effective tool for the nanocrystal characterization, especially for the determination of their chemical composition from the frequencies of the CdSe-like LO_1 phonon and the CdS-like LO_2 phonon [10-18]. Multiphonon Raman scattering in II-VI nanocrystals is much less studied, except for binary CdSe [19, 20] and CdS [21] quantum dots. For $CdS_{1-x}Se_x$ nanocrystals second-order Raman spectra were reported in several studies [12, 13, 22], but almost in each case the two-phonon Raman scattering was considered for only one mixed nanocrystal composition, in most of the cases the x value being within 0.33 to 0.37. In our earlier studies [8, 23], the second-order Raman spectra of $CdS_{1-x}Se_x$ nanocrystals were presented in a rather broad compositional interval, but the analysis was focused entirely on the first-order scattering.

Here we report on a targeted study of second- and third-order Raman scattering performed for an extensive series of samples of bulk and glass-embedded nanoscale $CdS_{1-x}Se_x$ crystals.

2. EXPERIMENTAL

Monocrystalline bulk $CdS_{1-x}Se_x$ samples were grown from the vapour phase. Nanoscale $CdS_{1-x}Se_x$ crystals were grown in borosilicate glass by well-known diffusion-limited growth technique similar to the one described earlier [7, 8].

Raman measurements were performed using a LOMO DFS-24 spectrometer with a FEU-79 phototube. The excitation was provided by an extensive set of laser lines of Ar^+, Kr^+, and He-Ne lasers ranging from 457.9 to 647.1 nm). For the samples with $CdS_{1-x}Se_x$ nanocrystals the measurements were performed at 295 K. The spectra of the monocrystalline samples were measured both at 77 and 295 K in different scattering configurations.

3. DISCUSSION

Raman scattering spectra of single $CdS_{1-x}Se_x$ crystals measured in off-resonance and resonance conditions are shown in Fig. 1 (a and b, respectively). In the off-resonance spectra (Fig. 1a), one can observe the first-order Raman peaks corresponding to the unpolar vibration of E_2 symmetry (40-42 cm^{-1}), the CdS-like LO-phonon peak of A_1 symmetry (298-305 cm^{-1}), and the CdS-like TO-phonon peak (234 cm^{-1}, only for CdS). Besides, in the same frequency range intense second-order maxima related to 2TA (87-108 cm^{-1}), TA+LA (near 130 cm^{-1}), and 2LA (214 cm^{-1} for $x = 0$) phonon scattering, are observed. It can clearly be seen that the compositional behaviour of these bands is far from straightforward, exhibiting for $x = 0.2$-0.3 an unexpected redistribution of intensities in the range 180-220 cm^{-1} and an appearance of a characteristic Fano antiresonance dip where (since is a solid solution system with the two-mode behaviour) one could expect the CdSe-related LO phonon peak to appear. Such compositional variation of the spectrum gives a clear evidence for an anharmonic coupling between vibrational states – the Fermi resonance, arising in case the levels of interacting one-phonon and two-phonon states being close in energy and the corresponding wavefunctions possessing the same symmetry [24].

The resonance Raman spectra of $CdS_{1-x}Se_x$ bulk crystals shown in Fig. 1b (in this case the Raman excitation wavelength was tuned in order to achieve the

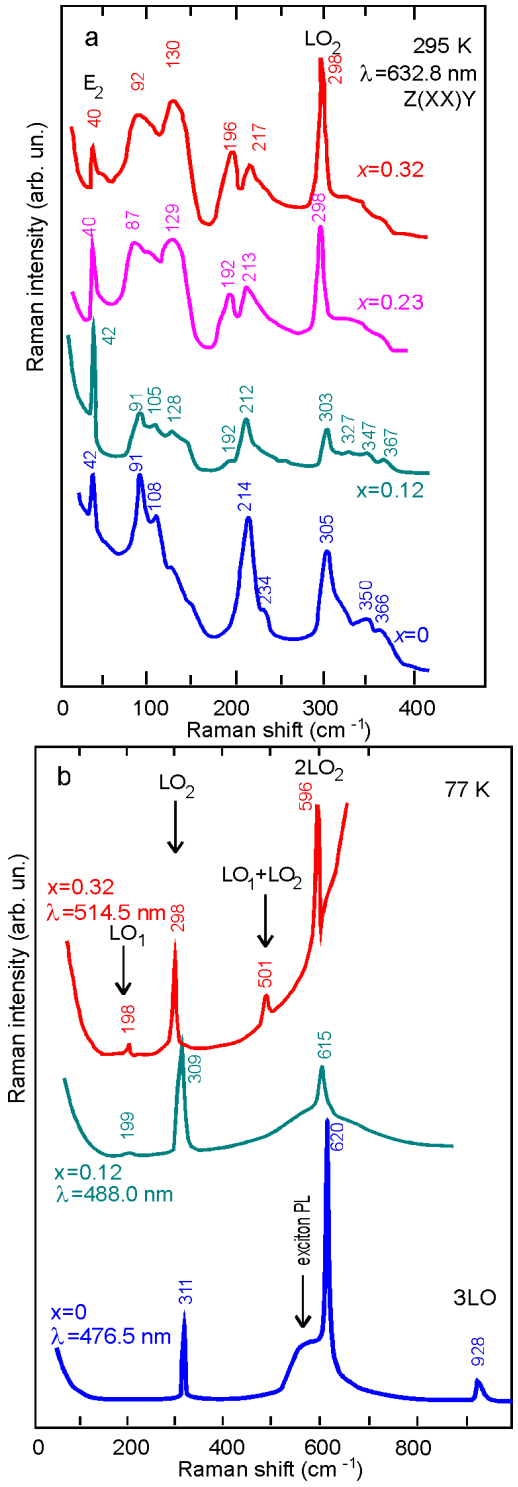

Fig. 1 – Raman scattering spectra of single $CdS_{1-x}Se_x$ crystals measured in off-resonance (a) and resonance (b) conditions

resonant matching with the mixed crystal band gap) exhibit a strong enhancement of the $2LO_2$ overtones and composite $LO_1 + LO_2$ phonon peaks with respect to the corresponding first-order Raman bands. Such behaviour is similar to that of binary II-VI semiconductors observed in the earlier studies [2, 3].

In case of a noticeable electron-phonon coupling the resonant Raman intensity can be expressed via the Fourier component of the retarded Green function [5]

$$I(\omega) \approx \mathrm{Im}\left[-\sum_{\nu,\mu} d_{n\nu} d^{*}_{n\mu} G^{\nu\mu}_{n}(\omega)\right] \tag{1}$$

where

$$G^{\nu\mu}_{n}(\omega) = \delta_{\nu\mu} G^{\nu}_{n}(\omega) \tag{2}$$

$$G^{\nu}(\omega) = -i\int_{0}^{\infty} dt \exp\left[i(\omega - \varepsilon_{n\nu} + i\gamma_{\nu}) + g_{n\nu}(t)\right] \tag{3}$$

$$g_{n\nu}(t) = N^{-1}\sum_{sq}\left|\chi^{n\nu}_{sq}\right|^{2}\Omega^{-2}_{sq}\left\{\left[n_{sq}+1\right]\exp(-i\Omega_{sq}t) + n_{sq}\exp(i\Omega_{sq}t) - \left[2n_{sq}+1\right]\right\} \tag{4}$$

$$\varepsilon_{n\nu} = E_{n\nu}(0) - N^{-1}\sum_{sq}\Omega^{-1}_{sq}\left|\chi^{n\nu}_{sq}\right|^{2} \tag{5}$$

is the energy of the electron excitation renormalized due to the electron-phonon coupling, Ω_{sq} are the phonon frequencies, n_{sq} are the corresponding occupation numbers, and $\left|\chi^{n\nu}_{sq}\right|$ are coupling constants. The positive value γ_{ν} characterizes the natural damping of $\varepsilon_{n\nu}$.

The strong electron-phonon coupling in bulk semiconductors, revealed in an enhancement of the LO phonon overtones in the resonance Raman spectra (Fig. 1b), occurs mostly with the participation of optical vibrations with wavelengths comparable to the size of the exciton [19]. The issue of the electron-phonon coupling on the nanoscale when the crystallite size is comparable with the exciton radius, can be discussed based on the resonance Raman studies of semiconductor nanocrystals.

Figure 2 demonstrates the resonant Raman spectra of glass-embedded $CdS_{1-x}Se_x$ nanocrystals measured at different excitation wavelengths. Note that the nanocrystals comprise only below 1 % of the sample catterin volume, hence resonant excitation conditions are required to obtain a detectable Raman signal. The CdSe-like LO_1 and CdS-like LO_2 phonon peak frequencies and intensities clearly depend on the nanocrystal composition. As can be seen from the figure, the observed divergence of the LO_1 and LO_2 phonon bands with decreasing x is accompanied by the decrease of the LO_1 phonon intensity and the increase of the LO_2 phonon peak. Therefore, Raman spectroscopy is often used for the compositional assessment of glass-embedded nanocrystals, based on the frequency difference [8, 10-15, 18] and intensity ratio [25] of the CdSe-like LO_1 and CdS-like LO_2 phonon peaks in the first-order Raman spectrum. This method is considered to provide the accuracy of $\Delta x \approx \pm 0.03$ [10, 15], being somewhat lower for the compositions close to CdSe and CdS due to the weakness of one of the phonon bands. Note that plotting the LO phonon frequency difference (instead of a direct consideration of the LO phonon frequency values) significantly reduces the errors of x determination resulting from the glass matrix pressure as well as possible systematic instrumental errors [15, 26]. Besides, it minimizes the role of confinement-related contribution of nonzero-wavevector phonons and surface phonon scattering revealed in the Raman spectra of nanocrystals [11-13, 15, 26].

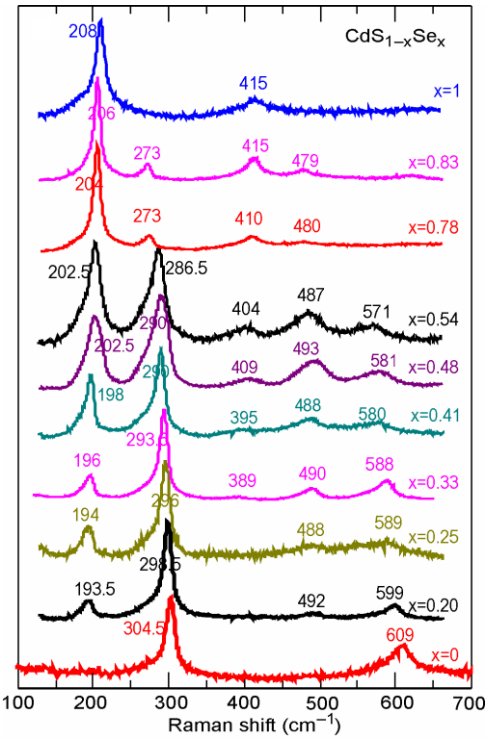

Fig. 2 – First- and second-order Raman spectra of $CdS_{1-x}Se_x$ nanocrystals of various compositions (a)

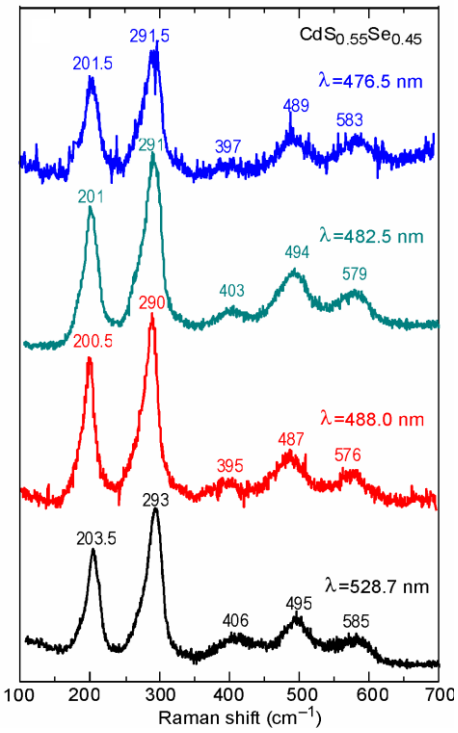

Fig. 3 – First- and second-order Raman spectra of the same sample with $CdS_{0.55}Se_{0.45}$ nanocrystals measured at room temperature at different excitation wavelengths

In the second-order spectrum, with decreasing x one can observe $2LO_1$ phonon peak weakening and downward shift (from 410 to 389 cm^{-1}) along with an increase of $LO_1 + LO_2$ (near 490 cm^{-1}, strong only for the samples with comparable content of S and Se) as well as (for noticeable S concentrations) $2LO_2$ phonon bands. The latter also exhibits an upward shift from 569 to 594 cm^{-1}. One should note that practically in all cases the overtone frequency is practically equal to the doubled LO phonon frequency (or the combination tone frequency is equal to the sum of the corresponding LO phonon frequencies). This, even with the account of a rather low dispersion of the phonon branches in CdS [27] and CdSe [28], indicates that the major contribution to the two-phonon Raman spectra is made by the near-zone-centre phonons. Similarly to the first-order Raman spectra, the difference of $2LO_2$ and $LO_1 + LO_2$ as well as $LO_1 + LO_2$ and $2LO_1$ phonon peak frequencies can serve a good measure of the glass-embedded nanocrystal composition.

Meanwhile, contrary to the bulk $CdS_{1-x}Se_x$ crystals (See Fig. 1b), the intensities of the second-order phonon bands in all cases are much lower than those of the first-order LO phonons. Moreover, while in the bulk crystals variation of the Raman resonance conditions by variation of the sample temperature or the excitation wavelength leads to a considerable redistribution of the first- and higher-order LO phonon peaks, it can be seen from Fig. 3 that in $CdS_{1-x}Se_x$ nanocrystals the corresponding intensity ratios remain practically the same under a broad variation of the excitation wavelength. This clearly indicates that, evidently, the electron-phonon coupling in $CdS_{1-x}Se_x$ nanocrystals is much lower than in the bulk crystals of the same system.

Note that in the Raman spectra of the glass-embedded $CdS_{1-x}Se_x$ nanocrystals we also observed third-order Raman scattering (Fig. 4). Earlier, the third-order Raman spectra were reported only for CdSe nanocrystals [13]. The third-order phonon peak intensities are even smaller than those of the two-phonon bands. This also supports our judgement on the weakness of the electron-phonon coupling in $CdS_{1-x}Se_x$ nanocrystals.

One should note that, similarly to our data, none of the earlier resonance Raman studies of $CdS_{1-x}Se_x$ nanocrystals reported on a noticeably different first-to-second order Raman peak intensity ratio with an increased contribution of two-phonon scattering in a way similar to the resonance Raman spectra of the bulk crystals. Still, different opinions were stated with regard to the electron-phonon coupling in the $CdS_{1-x}Se_x$ nanocrystals. An increase of the electron-LO-phonon coupling with increasing confinement was reported [22], however, this conclusion was based on a quite small variation of the second-to-first order LO phonon intensity ratio; moreover, the reported results do not seem reliable due to the very small nanocrystal size variation and the noisy spectra. In fact, all the scattered data reported before [12, 13, 23] exhibit the ratios of the two-phonon and one-phonon band intensities basically similar to ours, the examples of which are shown in Figs. 2 and 3. This conclusion on the electron-phonon coupling in $CdS_{1-x}Se_x$ nanocrystals being much weaker than in the corresponding bulk crystals is also supported by theoretical considerations. It is known that highly delocalized excitonic states of bulk semiconductors couple mainly to optical vibrations with wavelengths comparable to the exciton size [19]. As the electron and hole are confined in a smaller volume, the Fröhlich coupling becomes weaker since the electric field caused by the vibrations should be less effective in polarizing the exciton.

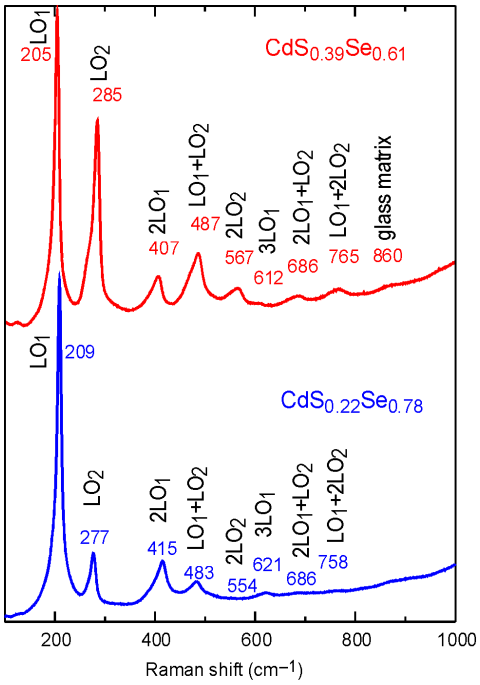

Fig. 4 – First-, second- and third-order Raman spectra of glass-embedded $CdS_{1-x}Se_x$ nanocrystals

4. CONCLUSIONS

Second-order Raman scattering spectra of bulk $CdS_{1-x}Se_x$ crystals at off-resonance excitation conditions are dominated by processes with the participation of acoustic phonons complicated by anharmonic resonant coupling of the two-phonon states with first-order optical phonons. Resonant Raman spectra of $CdS_{1-x}Se_x$ single crystals clearly show a strong enhancement of multiple LO phonon bands which strongly exceed in intensity the corresponding first-order LO phonon peaks. This is the evidence for the strong electron-phonon coupling in bulk $CdS_{1-x}Se_x$ crystals.

In the resonance Raman spectra of the glass-embedded $CdS_{1-x}Se_x$ nanocrystals, the multiple LO phonon bands are much weaker than the first-order ones. The corresponding intensity ratio reveals only a slight dependence on the nanocrystal composition, size, and excitation wavelength. The third-order Raman band intensities are even weaker. Therefore, one may concude on a much smaller electron-phonon coupling in the $CdS_{1-x}Se_x$ nanocrystals in comparison with the corresponding bulk materials.

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Раманівське розсіювання світла другого і третього порядку в об'ємних та вкраплених у скло нанометричних кристалах $CdS_{1-x}Se_x$

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Проведено вимірювання спектрів раманівського розсіювання світла другого і третього порядку в об'ємних та вкраплених у скло нанометричних кристалах $CdS_{1-x}Se_x$. За нерезонансних умов збудження у раманівських спектрах другого порядку об'ємних кристалів $CdS_{1-x}Se_x$ проявляється ангармонічна взаємодія оптичних фононів з двофононними станами з участю акустичних фононів. Спектри резонансного раманівського розсіювання монокристалів $CdS_{1-x}Se_x$, де проявляється сильне підсилення багатофононних LO смуг, свідчать про сильну електрон-фононну взаємодію в об'ємних кристалах $CdS_{1-x}Se_x$. Зі співвідношення інтенсивностей багатофононних і однофононних LO смуг у спектрах резонансного раманівського розсіювання вкраплених у скло нанокристалів $CdS_{1-x}Se_x$ зроблено висновок, що електрон-фононна взаємодія в нанокристалах набагато менша, ніж у відповідних об'ємних матеріалах.

Ключові слова: Раманівське розсіювання, Нанокристали, Електрон-фононна взаємодія.

Комбинационное рассеяние света второго и третьего порядка в объемных и внедренных в стекло нанометрических кристаллах $CdS_{1-x}Se_x$

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Проведены измерения спектров комбинационного рассеяния света второго и третьего порядка в объемных и внедренных в стекло нанометрических кристаллах $CdS_{1-x}Se_x$. При нерезонансных условиях возбуждения в спектрах комбинационного рассеяния второго порядка объемных кристаллов $CdS_{1-x}Se_x$ проявляется ангармоническое взаимодействие оптических фононов с двухфононными состояниями с участием акустических фононов. Спектры резонансного комбинационного рассеяния монокристаллов $CdS_{1-x}Se_x$, где проявляется сильное усиление многофононных LO полос, свидетельствуют о сильном электрон-фононном взаимодействии в объемных кристаллах $CdS_{1-x}Se_x$. Из соотношения интенсивностей многофононных и однофононных LO полос в спектрах резонансного комбинационного рассеяния внедренных в стекло нанокристаллов $CdS_{1-x}Se_x$ следует, что электрон-фононное взаимодействие в нанокристаллах намного меньше, чем в соответствующих объемных материалах.

Ключевые слова: Комбинационное рассеяние, Нанокристаллы, Электрон-фононное взаимодействие.

REFERENCES

1. O. Madelung, U. Rössler, M. Schulz, *Landolt-Börnstein – Group III Condensed matter, numerical data and functional relationships in science and technology, Vol. 41C.* (Springer: Berlin: 1982).
2. R.M. Martin, L.M. Falicov, *Resonant Raman scattering*. In: *Light scatering in solids I, Topics in Applied Physics, Vol. 8.* (Springer: Berlin: 1983).
3. R.C.C. Leite, J.F. Scott, T.C. Damen, *Phys. Rev. Lett.* **22**, 780 (1969).
4. I. Savatinova, M. Stefanova, *Spectrosc. Lett.* **8**, 993 (1975).
5. A.M. Yaremko, V.O. Yukhymchuk, V.M. Dzhagan, M.Ya. Valakh, Yu.M. Azhniuk, J Baran, H. Ratajczak, M. Drozd, *Semicond. Phys., Quantum Electron. & Optoelectron.* **10** No 2, 1 (2007).
6. A.M. Yaremko, V.O. Yukhymchuk, V.M. Dzhagan, M.Ya. Valakh, J. Baran, H. Ratajczak, *J. Phys: Conf. Ser.* **92**, 012061 (2007).
7. N.F. Borrelli, D. Hall, H. Holland, D. Smith, *J. Appl. Phys.* **61**, 5399 (1987).
8. Yu.M. Azhniuk, A.V. Gomonnai, Yu.I. Hutych, V.V. Lopushansky, I.I. Turok, V.O. Yukhymchuk, D.R.T. Zahn, *J. Cryst. Growth* **312**, 1709 (2010).
9. V. Dzhagan, N. Mel'nik, O. Rayevska, G. Grozdyuk, V. Strelchuk, O. Plyashechnik, S. Kuchmii, M. Valakh, *phys. status solidi* **5**, 250 (2011).
10. A. Tu, P.D. Persans, *Appl. Phys. Lett.* **58**, 1506 (1991).
11. A. Mlayah, A.M. Brugman, R. Carles, J.B. Renucci, M.Ya. Valakh, A.V. Pogorelov, *Sol. St. Commun.* **90**, 567 (1994).
12. A. Roy, A.K. Sood, *Phys. Rev. B* **53**, 12127 (1996).
13. A. Ingale, K.C. Rustagi, *Phys. Rev. B* **58**, 7197 (1998).
14. V.P.Kunets, V.O. Yukhymchuk, M.Ya. Valakh, *Semicond. Phys., Quantum Electron. & Optoelectron* **4** No 3, 196 (2001).
15. A.V. Gomonnai, Yu.M. Azhniuk, V.O. Yukhymchuk, M. Kranjčec, V.V. Lopushansky, *phys. status solidi b* **239**, 490 (2003).
16. A. Céreyon, A.-M. Jurdyc, V. Martinez, E. Burov, A. Pastouret, B. Champagnon, *J. Non-Cryst. Sol.* **354**, 3458 (2008).
17. B. Can Ömür, A. Aşıkoğlu, Ç. Allahverdi, M.H. Yükselici, *J. Mater. Sci.* **45**, 112 (2010).
18. E.S. Freitas Neto, S.W. da Silva, P.C. Morais, M.I. Vasilevskiy, M.A. Pereira-da-Silva, N.O. Dantas, *J. Raman Spectrosc.* **42**, 1660 (2011).
19. A.P. Alivisatos, T.D. Harris, P.J. Carrol, M.L. Steigerwald, L.E. Brus, *J. Chem. Phys.* **89**, 3463 (1990).
20. M.C. Klein, E. Hache, D. Ricard, C. Flytzanis, *Phys. Rev. B* **42**, 11123 (1990).
21. J.J. Shiang, A.N. Goldstein, A.P. Alivisatos, *J. Chem. Phys.* **92**, 3232 (1990).
22. G. Scamarcio, V. Spagnolo, G. Ventruti, M. Lugará, G.C. Righini, *Phys. Rev. B* **53**, R10489 (1996).
23. Yu.M. Azhniuk, A.G. Milekhin, A.V. Gomonnai, V.V. Lopushansky, V.O. Yukhymchuk, S. Schulze, E.I. Zenkevich, D.R.T. Zahn, *J. Phys.: Condens. Mat.* **16**, 9069 (2004).
24. M.P. Lisitsa, A.M. Yaremko, *Fermi Resonance* (Kyiv: Naukova Dumka: 1984) [in Russian].
25. W.S.O. Rodden, C.N. Ironside, C.M. Sotomayor Torres, *Semicond. Sci. Technol.* **9**, 1839 (1994).
26. Yu.M. Azhniuk, Yu.I. Hutych, V.V. Lopushansky, A.E. Raevskaya, A.L. Stroyuk, S.Ya. Kuchmii, A.V. Gomonnai, D.R.T. Zahn, *J. Phys.: Conf. Ser.* **78**, 012017 (2007).
27. M. Nusimovici, J.L. Birman, *Phys. Rev.* **156**, 925 (1966).
28. J. Camacho, A. Cantarero, *phys. status solidi b* **220**, 233 (2000).