

RESONANT INTERACTIONS AND DISORDER EFFECTS IN $\text{CdS}_{1-x}\text{Se}_x$ MIXED CRYSTALS RAMAN SPECTRA

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Anharmonic Fermi resonance between one-phonon and two-phonon states revealed in Raman spectra as well as resonant Raman scattering in $\text{CdS}_{1-x}\text{Se}_x$ mixed crystals are studied. The effect of compositional and radiation-induced disordering upon the observed spectral features is discussed. The irradiation-induced exciton photoluminescence band shift and redistribution of resonant Raman band intensities are related to the changes in the crystal electron subsystem under irradiation.

While studying Raman spectra in crystals resonant interactions between vibrational states due to the third- and fourth-order anharmonicity can be revealed. 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, is studied in detail in [1]. Spectroscopically anharmonic resonance is observed as essential redistribution of the interacting transition intensities and “repulsion” of the resonating levels. Investigations of mixed semiconductor crystals phonon spectra have revealed resonant anharmonic interaction between one- and two-phonon states in a number of systems, variation of the resonance conditions being achieved by changing the mixed crystal composition [2, 3] as well other factors, e. g. scattering angle while studying polariton Fermi resonance [4]. The important role is played by crystal lattice disordering taking place in mixed crystals due to fluctuations of the substituting isovalent atoms distribution. It results in the selection rules breakdown enhancing the anharmonic resonance in the phonon spectra. Additional lattice disordering can be caused by irradiation, especially with high-energy electrons, what is revealed in Raman features related to scattering processes with participation of phonons with non-zero wavevectors [5, 6].

A special interest is attracted to the studies of resonant Raman scattering when the frequency of the incident or the scattered light is close to the frequency of an electron transition in the crystal [7], since the electron subsystem of the crystal is known to be more sensitive to high-energy particle irradiation.

We report resonant interactions in the Raman spectra of $\text{CdS}_{1-x}\text{Se}_x$ ($0 \leq x \leq 0.35$) single crystals under high-energy electron irradiation. The samples were irradiated by 10-MeV electron beam with the fluence of 10^{16} to 10^{18} cm^{-2} . Raman spectra were measured by LOMO DFS-24 double-grating monochromator using He-Ne ($\lambda=632.8 \text{ nm}$) and Ar^+ ($\lambda=457.9, 488.0, \text{ and } 514.5 \text{ nm}$) lasers at 77 and 293 K.

$\text{CdS}_{1-x}\text{Se}_x$ mixed crystals Raman spectra at 293 K for XX-component of the scattering tensor, where vibrations of A_1 and E_2 symmetry are revealed [8], are shown in Fig. 1. Note that $\text{CdS}_{1-x}\text{Se}_x$ solid solutions are characterized by the two-mode type of the phonon spectrum compositional transformation, when in the mixed crystals spectra phonons with the frequencies close to those in both pure crystals – CdS and CdSe – are observed. At low concentrations of one of the components local vibrations of isovalent substituents can be observed in the spectra, which split into LO- and TO-phonons with the relevant component concentration increase.

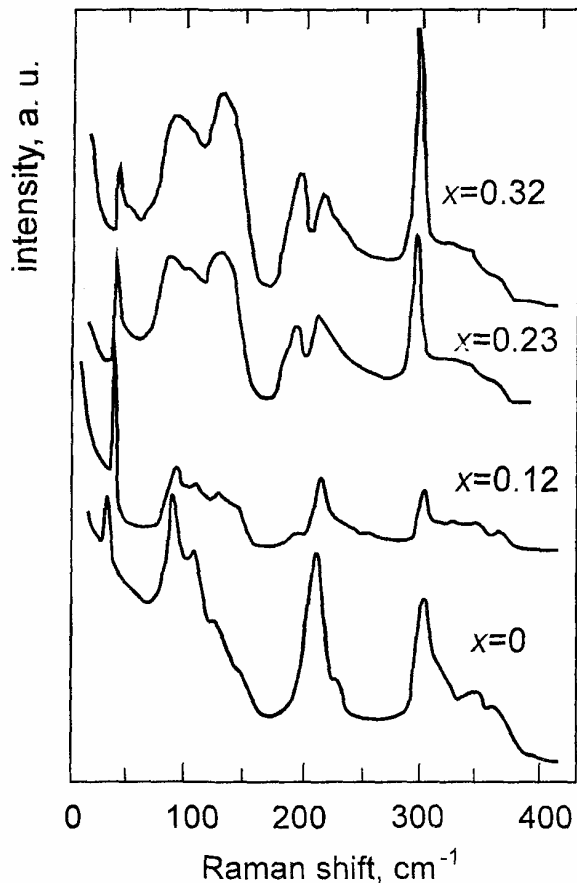


Fig. 1. Raman scattering spectra of $\text{CdS}_{1-x}\text{Se}_x$ crystals in $Z(\text{XX})Y$ geometry at 293 K, excited by He-Ne laser ($\lambda=632.8$ nm).

In pure CdS spectrum, as seen from Fig. 1, besides the first-order Raman peaks corresponding to unpolar vibration of E_2 symmetry (42 cm^{-1}), TO- and LO-vibrations of A_1 symmetry (234 and 305 cm^{-1} , respectively), intense maxima at 91 , 108 , 214 cm^{-1} and less pronounced features at 138 , 350 , and 366 cm^{-1} , related to two-phonon scattering processes, are observed. The low-frequency maxima at 91 and 108 cm^{-1} correspond to 2TA vibrations in different points of the Brillouin zone, the features at 138 and 214 cm^{-1} – to $\text{TA}+\text{LA}$ and 2LA vibrations, respectively, and the high-frequency bands (350 and 366 cm^{-1}) – to the two-phonon processes with optical and acoustic phonons participating.

In the mixed crystals at $x = 0.12$ a weak maximum at 192 cm^{-1} appears, its frequency being close to that of selenium atom local vibration in CdS crystal (188 cm^{-1} [9]). With the increase of selenium concentration in the

solid solution with two-mode compositional transformation of the phonon spectrum the local vibration band should split into TO_1 and LO_1 bands, corresponding to the vibration of selenide component of the mixed crystal. However, in this case no splitting with x is observed, instead the discussed band considerably increases in intensity and somewhat shifts in frequency (196 cm^{-1} at $x = 0.32$). Meanwhile the two-phonon maxima intensity in the range of 130 to 212 cm^{-1} strongly increases, their shape becoming asymmetric with pronounced dips between the discussed maxima, typical for Fano antiresonance [1].

Such complicated compositional behaviour of the spectrum in a narrow interval of x is typical for anharmonic Fermi resonance. In this case with the increase of Se concentration TO_1 i LO_1 phonon frequencies fall into the frequency range of $\text{TA}+\text{LA}$ and 2LA excitations, respectively. The “repulsion” of the interacting vibrations energy levels results in the fact that in experiment TO_1 and LO_1 phonon bands are not observed explicitly, the 192 cm^{-1} band frequency remains practically unchanged in the composition interval under investigation, and on its either side the redistribution of intensities of the interacting states results in typical antiresonance dips.

Note that in solid solutions an additional factor, enhancing the anharmonic coupling of phonon states, lies in the selection rules breakdown due to compositional disordering. From this point of view it was especially interesting to study the effect of additional disorder due to high-energy electron irradiation upon $\text{CdS}_{1-x}\text{Se}_x$ crystals Raman spectra. No noticeable changes in the spectroscopic manifestation of Fermi resonance in this system was found after irradiation with the electron fluences up to 10^{18} cm^{-2} . Evidently, this is related to the fact that frequencies and widths of the interacting phonon excitations as well as the anharmonicity coefficients, which are the main factors, responsible for the anharmonic resonance, are much more dependent on the fluctuations of S and Se substituents local environment than on the amount of irradiation-induced defects.

However, resonant Raman scattering spectra, where $\text{CdS}_{1-x}\text{Se}_x$ crystal electron subsystem participates as well, could be expected to be more sensitive to radiation-induced disordering of the crystal.

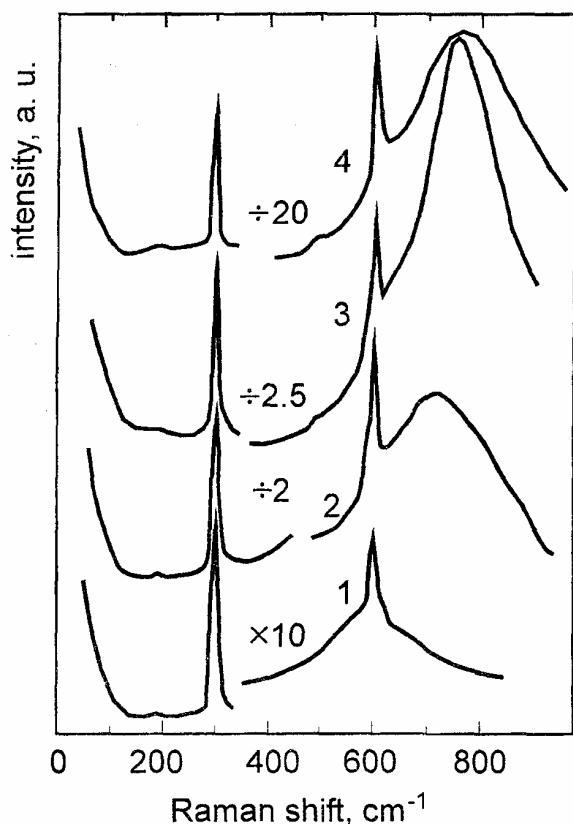


Fig. 2. Resonant Raman scattering spectra of $\text{CdS}_{0.88}\text{Se}_{0.12}$ crystal, irradiated with the fluence Φ of 10-MeV electrons: $\Phi = 0$ (1), $3 \times 10^{16} \text{ cm}^{-2}$ (2), $3 \times 10^{17} \text{ cm}^{-2}$ (3), 10^{18} cm^{-2} (4).

Resonant Raman spectra of $\text{CdS}_{0.88}\text{Se}_{0.12}$ single crystals, irradiated with 10-MeV electrons, are shown in Fig. 2. As seen from the figure, in the non-irradiated sample spectrum LO_1 (199 cm^{-1}) and LO_2 (310 cm^{-1}) phonon peaks are observed as well as 2LO_2 peak at the frequency 615 cm^{-1} , revealed at the background of a broader maximum, related to the radiative recombination of free A_1 exciton (curve 1). Note that the ratio of phonon band intensities, corresponding to the sulphide and selenide components of the solid solution, is much higher than the corresponding atoms concentration ratio $x/(1-x) \approx 7.5$. This is related to the fact the Raman scattering cross-section being strongly determined by the constant of electron-phonon

interaction (polaron constant) α . For two-mode II-VI solid solutions in the model of two non-interacting oscillators the polaron constant values for the mixed crystal components is evaluated from [10]

$$\alpha_i = \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_\infty + 4\pi\rho_i} \right) \frac{2\pi e^2}{h} \left(\frac{m^*}{2h\nu_{\text{LO},i}} \right), \quad (1)$$

ε_0 and ε_∞ being static and high-frequency dielectric permeability, e and m^* – elementary charge and effective mass of an electron, $4\pi\rho_i$ – oscillator strengths, $h\nu_{\text{LO},i}$ – corresponding LO phonon energies. For the solid solutions under investigation $\alpha_2(\text{CdS})/\alpha_1(\text{CdSe}) \approx 1.7$ [10], hence at resonant excitation conditions the additional enhancement of the bands, corresponding to LO_2 phonons of the mixed crystal sulphide component, is observed.

After irradiation a maximum at 506 cm^{-1} due to $\text{LO}_1 + \text{LO}_2$ phonon scattering is observed as well as the 2LO_2 phonon band intensity increase. This is accompanied by red shift of the exciton luminescence band as well as its intensity increase with Φ (curves 2–4). For the maximal fluence of electrons $\Phi = 10^{18} \text{ cm}^{-2}$ 2LO_2 to LO_2 phonon intensity ratio increases by factor of about 400.

Such behaviour is the evidence for the disorder-induced variation of the conditions of resonance between the energy of the incident (scattered) light and the energy of a characteristic electron transition in $\text{CdS}_{0.88}\text{Se}_{0.12}$ crystal under electron irradiation. Note that in the mixed crystal system under investigation the compositional disorder effect is maximal in the range of $x = 0.1 \div 0.2$ [11]. As noted above, the radiation-induced disorder does not affect first- and second-order Raman spectrum and is not essential for the phonon subsystem of the crystal. However, the effect of irradiation upon the electron subsystem is revealed in resonant Raman spectra what is, in our opinion, related to the radiation-induced density-of-states tails due to the formation of fluctuation levels near the bottom of the conduction band and the top of the valence band caused by large-scale fluctuations of potential induced by the crystal lattice disordering. This results both to some shift of the

A_1 exciton recombination band and the redistribution of first- and second-order resonant Raman scattering intensities. Note that even in this range of x , where the density-of-states tails are the longest [11, 12], we have not detected any radiation-induced changes in the absorption spectra and in the spectral position of the known “green”, “orange” and “red” photoluminescence bands in $CdS_{1-x}Se_x$ single crystals [13].

Thus, the reported studies have revealed anharmonic resonance of one- and two-phonon excitations in compositionally disordered $CdS_{1-x}Se_x$ single crystals. Disordering of these crystals under high-energy electron irradiation, observed in resonant Raman scattering and exciton photoluminescence spectra, is related to the radiation-induced tails of density of electron states.

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РЕЗОНАНСНІ ВЗАЄМОДІЇ ТА ЕФЕКТИ РОЗУПОРЯДКУВАННЯ У СПЕКТРАХ КОМБІНАЦІЙНОГО РОЗСІЮВАННЯ ЗМІШАНИХ КРИСТАЛІВ $CdS_{1-x}Se_x$

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Досліджено ангармонічний резонанс Фермі між однофоновими і двофоновими станами, що проявляється у спектрах комбінаційного розсіювання, а також резонансне комбінаційне розсіювання світла у змішаних кристалах $CdS_{1-x}Se_x$. Обговорюється вплив композиційного і радіаційного розупорядкування на спектральні особливості. Індуковане опроміненням зміщення смуги екситонної фотолюмінесценції та перерозподіл інтенсивностей резонансного комбінаційного розсіювання пов'язуються зі змінами в електронній підсистемі кристала під дією опромінення.