Exciton-phonon interaction in crystals and quantum size structures

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Abstract. In this report, the problem of electron-phonon interaction (EPI) in bulk semiconductors and quantum dots (QDs) is considered. It is shown that the model of strong EPI developed for organic molecular crystals can be successfully applied to bulk and nano-sized semiconductors. The idea of the approach proposed is to describe theoretically the experimental Raman (IR) spectra, containing the phonon replicas, by varying the EPI constant. The main parameter of the theoretical expression (β), is the ratio of EPI constant (χ) to the frequency of the corresponding phonon mode (Ω).

Theoretical results show that variation of the QD size can change the value of χ.

1. Introduction
One of the important characteristics of both bulk and nano-sized system is the electron-phonon interaction strength. The response of the physical system to the action of electromagnetic wave is known to be dependent on the EPI strength. The EPI can be characterized as weak or strong depending on the ratio of the EPI constant (χ) to the corresponding phonon frequency (Ω); β = χ / Ω.

The spatial confinement of electrons and phonons in nanostructures has a crucial effect on their properties [1]. The influence of the spatial confinement on the EPI value has been studied theoretically [1-3] and experimentally [1, 4, 5]. However, there exist discrepancies in the results obtained concerning the value of the EPI, and no clear conception has been formed in this issue yet.

In view of all stated above, the problem of variation of the EPI value under evolution of semiconductor from bulk to nanostructures of different size is approached once more in this report.

Theoretical consideration of the EPI in bulk semiconductor crystals is often limited to perturbation theory and describes first and second phonon replicas in Raman or IR spectra [6]. In the case of organic crystals, including those with hydrogen bonds, this approach is not sufficient because they are frequently characterized by β > 1 which causes multiphonon replicas. This circumstance has been emphasized as early as in the works of Davydov and coworkers [7].
2. General approach
The idea of our approach is to describe theoretically the experimental Raman (IR) spectrum, containing multiphonon replicas, by varying $\beta_3$ value and to conclude on the EPI strength from the value of $\beta_3$ at which the best fitting of the experimental spectra is achieved. Theoretical description of spectra is convenient to be made by using the theory of strong EPI which allows one to consider the contribution of several phonons to the spectrum by using a single expression.

In semiconductor crystals photoexcited electron in the conduction band and hole in valence band, according to Wannier’s model, are separated by a distance $R_{ex}$ and interaction of phonons with each kind of carriers is considered separately.

For molecular crystals the photoexcited electron-hole pair is located on the same atom or molecule. Therefore the phonons interact with this pair (Frenkel exciton) and one can say about exciton-phonon interaction.

Here we study CdS$_x$Se$_{1-x}$ quantum dots (QD) of ~3-5 nm diameter, which are similar to big molecules. Therefore the theoretical approach developed for molecular type crystals can be enough adequate for such QD structures too. Moreover our calculations show that Raman spectra of bulk semiconductor crystals, for which exciton maxima are clearly defined within this approach, are also described well enough. (Problem of EPI for crystals with broad electron bands will be considered in detail elsewhere).

3. Theoretical relations
We give below only a final expression describing energy and intensity of the peaks in vibrational spectrum for the case of strong electron-phonon interaction (for more details see [8, 9]). When the energy band is narrow enough, this expression is obtained in the following approximation:

$$H = \sum_{n,v} \varepsilon_{nv} A^+_v A_n + \sum_{s,q} \Omega_{sq} \beta_{sq} \beta_{sq}^*$$

(1)

$$\varepsilon_{nv} = E_{nv}(0) - N^{-1} \sum_{s,q} |\chi_{sq}^{nv}|^2$$

(2)

Where $\varepsilon_{nv}$ is an energy of electron excitations, $E_{nv}(0)$, renormalized due to the electron-phonon interaction.

The intensity of Raman scattering (or IR) can be expressed by the Fourier component of the retarded Green function from exciton, $A_n, A^+_v$, and phonon, $\beta_{sq}, \beta_{sq}^*$ operators [9]:

$$I(\omega) \approx \text{Im} \left[ -\sum_{r,\mu} d_{rv}^* d_{\mu v}^+ G^{\mu v}_r(\omega) \right], \quad G^{\mu v}_n(\omega) = \delta_{\mu v} G^{\nu \nu}_n(\omega)$$

(3)

$$G^{\nu \nu}_n(\omega) = -i \int_0^\infty dt \exp[i(\omega - \varepsilon_{nv} + i\gamma_v) + g_{nv}(t)]$$

(4)

In Eq. (4), the positive value of $\gamma_v$ means a natural damping of an excitation with energy $\varepsilon_{nv}$; $d_{nv}$ is a dipole moment (or susceptibility); $g_{nv}(t)$ is a complex function depending on the lattice frequencies $\Omega_{sq}$ as well as on the coupling constants $\chi_{sq}^{nv}$ and is determined as

$$g_{nv}(t) = N^{-1} \sum_{s,q} \left[ \Omega_{sq}^{nv} \left( n_{sq} + 1 \right) \exp(-i\Omega_{sq} t) + n_{sq} \exp(i\Omega_{sq} t) - [2n_{sq} + 1] \right]$$

(5)

Where $n_{sq}$ is the occupation number of the vibration state with the frequency $\Omega_{sq}$.

In the numerical analysis we neglect the dependence on the wave vector $q$ in Eqs. (3-5) by putting $\Omega_{sq} = \Omega_s$ for the lattice phonon frequencies and $\chi_{sq}^{nv} = \chi_s^{\nu \nu}$ for the coupling constants, where $v$ numerates the electron states and $s$ denotes the phonon branch.
4. Experimental results and discussion

The samples studied were CdS$_x$Se$_{1-x}$, CdSe and CdS quantum dots (QDs) embedded in a borosilicate glass matrix as well as bulk CdS and CdS$_x$Se$_{1-x}$ crystals with composition $x$ close to that in the QDs.

Raman spectra were measured with a DFS-24 double grating spectrometer (LOMO) at room temperature. Discrete lines of an Ar$^+$-laser were used for the excitation. The signal was registered with a photomultiplier working in the photon counting mode. The known frequencies of the discharge lines of the Ar$^+$-laser served for a precise measurement of the Raman band frequencies.

Figure 1 (a) (curves 1) shows the experimental Raman spectrum from CdS$_{0.37}$Se$_{0.63}$ QDs ($d$=5 nm) in the borosilicate matrix and the corresponding theoretical modeling. The first-order Raman spectrum of CdS$_{1-x}$Se$_x$ solid solutions is known to comprise two main modes: CdSe-like and CdS-like. Beside them, the overtones of CdSe-like and CdS-like LO vibrations as well as mixed second order bands can appear in the spectrum. For QDs of the same composition $x$ the frequencies can differ from the bulk values due to the effects of phonon confinement and matrix-induced hydrostatic stress. For bulk crystals, the frequency and intensity of all the bands depend only on the alloy composition $x$. The results of fitting the Raman spectrum of a bulk CdS$_{0.37}$Se$_{0.63}$ crystal are given in Figure 1 (b).

![Figure 1](image-url)

**Figure 1.** Results of modelling the Raman spectra of QD (a) and bulk (b) CdSe$_x$Se$_{1-x}$.

The results of theoretical fitting of the experimental Raman spectra, shown in Figure 1, were obtained by variation of the value of EPI constant $\chi_S$. It is seen from Figure 1 (curves 1) that good enough fitting is achieved simultaneously for both first-order and second-order bands as well as for those corresponding to sums and differences of the first-order phonon frequencies. The shape of the theoretical curve is crucially determined by the value of $\beta_S = \chi_S / \Omega_S$ equal to 1.01 and 1.03 for the CdSe-like and CdS-like modes, respectively.

Figure 1a (curves 2) shows experimental and theoretical spectra for CdS$_{0.9}$Se$_{0.1}$ QDs ($d$=3 nm). Due to the low Se-concentration, the spectrum is dominated by the CdS-like peak and its replicas, with the best fitting being achieved at $\chi_S / \Omega_S$ =1.82.
In Figure 2, as an example, modeling of the experimental Raman spectrum of bulk CdS, taken from Ref. [10], is presented. It is clearly seen that several first peak intensities are well fitted by using only one coupling constant $\chi_S^v$ parameter (lattice frequencies $\Omega_S=304$ cm$^{-1}$, $\chi_S/\Omega_S=2.6$). But for 5th and higher peaks the effect of electron band width on intensity of peaks is important (this situation will be discussed in detail elsewhere).

5. Conclusions
A method of estimation of the magnitude of EPI in semiconductor nanostructures is proposed. The method is based on the application of the model of strong EPI to describe the experimental Raman (IR) spectra. The method allows to describe theoretically the experimental Raman (IR) spectrum, containing multiphonon replicas, by varying $\beta_S$ value and to conclude about the EPI magnitude from the value of $\beta_S$ at which the best fitting of the spectra is achieved. The method developed can be applicable not only to polar semiconductors, but also for covalent ones like Si and Ge.

References
[1] Mitin V V, Kochelap V A and Stroscio M A 1999 Quantum heterostructures. Microelectronics and Optoelectronics, Cambridge University Press, Cambridge
[2] Klein M C, Hache F, Ricard D and Flytzanis C 1990 Size dependence of electron-phonon coupling in semiconductor nanospheres: The case of CdSe Phys. Rev. B. 42 11123
[3] Chamorro M, Gourdon C, Lavallard P, Lublinskaya O and Ekmov A 1996 Phys. Rev. B. 53 1336
[4] Spagnolo V, Venturi G, Scamarcio G, Lugara M and Righini G 1995 Enhancement of electron-hole exchange interaction in CdSe NCs: quantum confinement effect Superl. & Microstr. 18 113
[5] Cardona M and Guntherodt G 1991 Light Scattering in Solids VI, Springer Verlag, Berlin: 431
[6] Zeyher R 1975 Theory of multiphonon raman spectra above the energy gap in semiconductors Solid State Commun. 16 49
[7] Davydov A S 1968 Theory of Molecular Excitons, Nauka, Moscow
[8] Ratajczak H and Yaremko A M 1999 Theory of the profiles of hydrogen stretching infrared bands of hydrogen-bonded solids: Fermi resonance effect and strong coupling between the high-frequency hydrogen stretching vibration and low-frequency phonons Chem. Phys. Lett. 314 122
[9] Yaremko A M, Ratajczak H, Baran J, Barnes A, Mozdor E V and Silvi B 2004 Theory of profiles of hydrogen bond stretching vibrations: Fermi-Davydov resonances in hydrogen-bonded crystals Chem. Phys. 306 57
[10] Leite R C C, Scott J F and Damen T C 1969 Multiple-Phonon Resonant Raman Scattering in CdS Phys. Rev. Lett. 22 780