



Origin of the temperature dependence of the band gap of PbS and PbSe quantum dots

P. Dey^a, J. Paul^a, J. Bylsma^a, D. Karauskaj^{a,*}, J.M. Luther^b, M.C. Beard^b, A.H. Romero^{c,d}

^a Department of Physics, University of South Florida, 4202 East Fowler Avenue, Tampa, FL 33620, USA

^b National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401, USA

^c Max-Planck-Institute für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

^d Physics Department, West Virginia University, Morgantown, WV 26506-6315, USA

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ABSTRACT

The lead chalcogenides semiconductor materials show in the bulk a shift of the electronic band gap with temperature that is opposite to the majority of direct or indirect band gap semiconductors, namely they show a decreasing of the band gap energy with decreasing temperature. However, in the nanocrystalline form a peculiar behavior has been observed. The shift of the band gap energy with temperature depends on the diameter of the quantum dots, and for sufficiently small quantum dots, the energy shift of the band gap becomes flat and even switches sign, following the behavior of conventional semiconductors. In this manuscript, the temperature dependence of the electronic band gap of PbS and PbSe semiconductor nanocrystals of different diameter was carefully measured. The observed behavior can be reproduced using a simple two-oscillator model used previously in bulk semiconductors without the need to invoke complicated schemes. Furthermore, *ab initio* calculations of the phonon density of states of nanocrystals with increasing diameters provide fascinating insights into the embryonic phase of solids. At small cluster sizes, the vibrations are quite localized and little dispersion is noted, as it is expected for almost molecular systems. However, as the nanocrystal size increases to 10 Å radius, the vibrational spectra become broader and starts to be quite similar to the bulk.

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1. Introduction

In bulk semiconductors the temperature dependence of the band gap is primarily a consequence of the renormalization due to electron–phonon interactions, and to a lesser extent, the thermal expansion of the lattice. In most semiconductors the electron–phonon interactions lead to an increase of the band gap energy with decreasing temperature, due to a decrease in the phonon population. Isotopic engineering of semiconductors has lead to accurate measurements of the zero Kelvin renormalization of the band gaps due to electron–phonon interactions [1]. However, the family of lead salt semiconductors PbS, PbSe, and PbTe, show the reversed behavior, i.e., the band gap energy decreases with decreasing temperature [2–6]. In addition to the lead salts, CuCl, CuBr, CuI and some ternary chalcopyrites containing Ag and Cu show this dependency [7,8]. This behavior is counterintuitive with what is known from a large number of semiconductor materials. Early calculations succeeded in explaining the observed behavior in PbTe as an interplay between the effect of the electron–phonon

renormalization and the lattice expansion. The thermal expansion contribution was thought to have an anomalous sign and contribute about half of the measured temperature dependence of the gap [9]. The same approach was used on PbSe semiconductor but had only limited success [10]. The peculiar behavior of the temperature dependence of the band gap of these bulk semiconductors is not yet well understood.

The advent of nanotechnology has lead to renewed attention to understanding the fundamental interactions of these materials, primarily because of the ability to synthesize very high quality colloidal quantum dots and possible applications. The most exciting application has been the prospect of using these nanomaterials in solar cell devices in order to achieve enhanced photocurrents [11–14]. Therefore, understanding the fundamental electron–phonon interactions that govern the optical and transport properties of these nanomaterials is of crucial importance. However, the high quantum confinement in PbSe and PbS colloidal quantum dots seemed to further complicate the already unusual behavior of the band gap with temperature observed in the bulk. In the first and most important study, the temperature dependence of the band gap was measured for different diameter PbS and PbSe quantum dots [15]. The temperature dependence of the band gap showed very strong size dependence. The magnitude of the energy shift of

* Corresponding author. Tel.: +1 8139740457.

E-mail address: karauskaj@usf.edu (D. Karauskaj).

the band gap with temperature in PbS and PbSe quantum dots decreased with decreasing diameter size, and for small enough diameters, it changed sign. The energy shifts were given as dE/dT values, which is valid for the temperature range where the temperature dependence of the band gap can be approximated to be linear. The measured values of dE/dT were thought to be dominated by lattice dilation and interband electron–phonon terms, altered by the strong quantum confinement. However, several contributions were taken into account to quantitatively reproduce the energy shift of the band gap, including thermal expansion of the lattice, thermal expansion of the wave-function envelope, mechanical strain, and electron–phonon coupling. In a more recent study, the cause of the aforementioned sign change in the band gap energy shift with temperature was attributed to a strong temperature dependence of the effective mass, which leads to a strong temperature dependence of the confinement energy [16].

The temperature dependence of the band gap at constant pressure can be separated into harmonic and anharmonic contributions: $(\partial E_g/\partial T) = (\partial E_g/\partial T)_{\text{har}} + (\partial E_g/\partial T)_{\text{anhar}}$. The harmonic term arises from the electron–phonon interaction, while the anharmonic term is due to the thermal expansion [17,18]. In most semiconductors, the contribution from the thermal expansion is smaller and can be neglected in the first approximation. The temperature dependence of the band gap can be obtained to first approximation by evaluating the harmonic term. The evaluation of the harmonic term is quite challenging, therefore, approximate models have shown to be very useful tools in the evaluation of the temperature dependence of the band gap of solids [19,20]. The first approximate model describing the energy shift with temperature in bulk semiconductors was introduced by Varshni and has been extensively used in the literature [21]. However, this model predicts a $\sim T^2$ dependence of the band gap at low temperature and does not reproduce the $\sim T^4$ dependence measured for bulk silicon [22]. In the present study, a model introduced by Viña et al. [19] is used. This model has successfully reproduced the temperature dependence of the band gap of numerous bulk semiconductors [1,23] and has recently been adopted to semiconducting single-walled carbon nanotubes which exhibit strong quantum confinement [24,25], and several semiconductors with chalcopyrite structure, which exhibit a rather peculiar nonmonotonic temperature dependence of the energy gap [8].

The electron–phonon interaction depends critically on the amplitude of the phonons and the corresponding coupling constants. Unfortunately, calculations of the corresponding electron–phonon interaction coefficients are difficult and rare. The phonon density of state is however accessible with great precision from *ab initio* calculations. In the present work, *ab initio* calculations were performed for different size nanoclusters up to the point where the phonon density of states resembles that of the bulk, providing insights into the embryonic phase of the formation of solids. Two average phonon energies were retrieved from the phonon density of states and used in the two oscillator model. The band gap energy shift of the PbS and PbSe nanocrystals for different diameters was successfully modeled using the two-oscillator model.

2. Experiment

Absorption data from these high quality drop cast films were used to obtain the temperature dependence of PbS and PbSe quantum dots. The samples were held in vacuum in a liquid helium cryostat and the temperature was maintained through the combined effect of helium vapor cooling and heating using a

temperature controller. The data was collected using a DA3 Fourier transform infrared spectrometer equipped with indium antimonide and silicon photodiodes. The quantum dot studied here have been characterized thoroughly in terms of relating the diameter size to the 1s exciton absorption energy using different techniques including TEM images [26–30]. The data presented in Ref. [26] is typical of the characterization studies performed routinely on our samples. However, accurate empirical models have been developed, which relate the diameter size with the 1s exciton absorption energy based on characterization studies performed over the past decades [29,30]. We have used the empirical model proposed in Ref. [30] to relate the 1s exciton absorption to the diameter size.

3. Results and discussion

The temperature dependence of the band gap has been measured for a variety of quantum dots including CdSe, InAs, Si, and GaAs [31,32]. In general, the dependence of the band gap with temperature follows the behavior seen in the bulk, where the magnitude of the energy shift in quantum dots might be somewhat reduced as compared to the bulk. The present study started with CdSe quantum dots, a semiconductor material that behaves according to the known behavior in the bulk, i.e., an increase of the band gap energy with decreasing temperature. As it is typical, the band gap energy here is defined as the energy of the lowest 1s exciton. The 1s exciton energy is somewhat reduced by the exciton binding energy but follows the band gap energy shift with temperature very closely. Very minute changes of the exciton binding energy with temperature can be neglected. The data for CdSe quantum dots are not shown here, but for different quantum dot diameters the shifts of the band gap with temperature were very close to the bulk values, showing little diameter dependence and confirming previous studies [16].

We further proceed with a systematic study of the energy shift of the band gap with temperature for the lead chalcogenide quantum dots PbS and PbSe. In Fig. 1(a) several representative absorption spectra of the 1s exciton state in PbS quantum dots at different temperatures are shown. They are typical of all the quantum dots studied. In addition to the energy shift with temperature, a substantial reduction in broadening with decreasing temperature is observed, despite the large inhomogeneous linewidth due to the size distribution of the quantum dots. Based on the observation that in most cases the quantum dots follow the band gap temperature behavior of their bulk materials, we begin our attempt to understand the strong size effect of PbS and PbSe quantum dots using models that have successfully reproduced the bulk energy shifts. Recently, a direct comparison between bulk PbS of natural composition and isotopically enriched Pb^{34}S observed virtually no net renormalization of the band gap due to zero point motion at low temperature [33]. This rather surprising behavior could only be explained as a cancelation of the contributions between the Pb and S vibrations. A multi-oscillator model was used, similar to the models used previously, where contributions from ‘Pb-like’ and ‘S-like’ vibrations were included with *opposite sign*. In these studies phonon frequencies were obtained from the phonon density of state which was obtained from *ab initio* calculations [34]. The interplay between the ‘Pb-like’ and ‘S-like’ vibrations persist at higher temperature as well and this model reproduced both, the absence of zero Kelvin renormalization and the overall temperature dependence of the band gap of bulk PbS.

Similar to the bulk studies, we used a two oscillator model to reproduce the temperature dependence of the band gap of PbS quantum dots based on models used previously, where the sign of the ‘Pb-like’ and ‘S-like’ contributions are opposite [33]. As pointed out in Ref. [1] two oscillator models are justified in binary

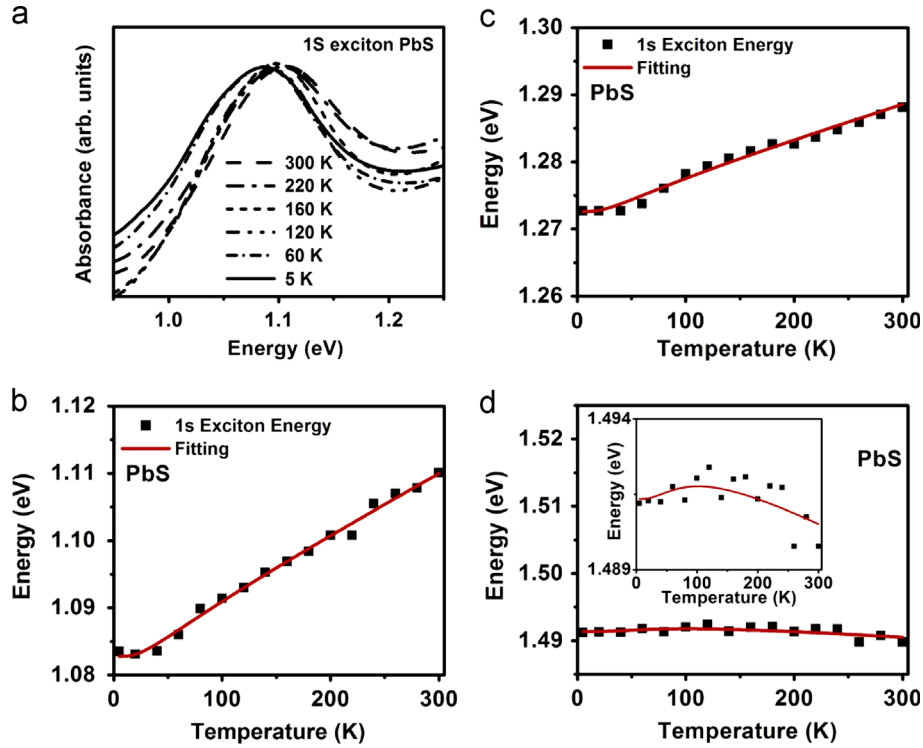


Fig. 1. (Color online) (a) The 1s exciton absorption peak of PbS quantum dots for different temperatures. In addition to the energy shift with temperature, a reduction of the linewidth with decreasing temperature can be observed. (b)–(d) Temperature dependence of PbS quantum dots for different diameters $d \approx 3.8$ nm, $d \approx 3.2$ nm, and $d \approx 2.8$ nm, respectively. Squares are the experimental data whereas the red (grey) line is the fitting. (b)–(d) are plotted at the same 40 meV energy axis for ease of comparison. The inset of (d) shows the temperature dependence of the band gap of the same diameter PbS quantum dots on a 5 meV (1.489–1.494 eV) energy scale.

semiconductors, especially those in which cation and anion masses are very different. The use of the two oscillator model has lead to an improved fit of the temperature dependence of the band gap of these materials [1]. In the absence of more detailed information about the exact effect of thermal expansion, we consider only the net contribution of electron–phonon interactions and the change in lattice constant combined, since both of these terms have a similar dependence on the phonon population factors, the vibrational amplitudes, and the atomic masses. Exactly the same model was used to fit the temperature shift of PbSe quantum dots, applying the same principle of ‘Pb-like’ and ‘Se-like’ phonons having contributions of opposite sign

$$E_g = E_0 + E_1 \left[2 \left(\exp \left(\frac{f_1}{kT} \right) - 1 \right)^{-1} + 1 \right] - E_2 \left[2 \left(\exp \left(\frac{f_2}{kT} \right) - 1 \right)^{-1} + 1 \right] \quad (1)$$

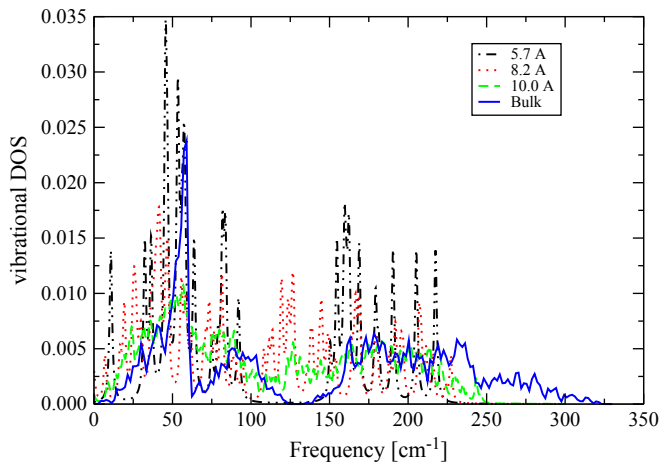
The phonon frequencies were obtained from predominant peaks in the phonon density of states attained from the *ab initio* calculations for bulk PbS [34] and PbSe [35], respectively. The calculated phonon density of states for bulk PbS and PbSe does show two distinct regions that can be attributed to ‘Pb-like’ vibrations at low frequency, and either ‘S-like’ or ‘Se-like’ vibrations at higher frequency. The average phonon frequencies used are $f_1 = 50 \text{ cm}^{-1}$ (6.06 meV) and $f_2 = 235 \text{ cm}^{-1}$ (29.1 meV) for PbS. The experimental data together with best fits are shown in Fig. 1 (b–d) for PbS quantum dots of diameters $d \approx 3.8$ nm in (b), $d \approx 3.2$ nm in (c), and $d \approx 2.8$ nm in (d), respectively. The value of E_0 is determined by the band gap energy of the bulk PbS semiconductor and the quantum confinement effect on the exciton energy. The values E_0 , E_1 and E_2 are varied for best fitting and provided in Table 1. The magnitude of both E_1 and E_2 coefficients decreases with decreasing diameter, but E_1 corresponding to low frequency ‘Pb-like’ vibrations decreases faster. The interplay

between the low frequency ‘Pb-like’ and higher frequency ‘S-like’ phonons is sufficient in explaining the decrease of the band gap energy shift with temperature which become almost flat for the $d \approx 2.8$ nm diameter dots. The inset of Fig. 1(d) shows a minor sign switch of the of the band gap shift which can also be reproduced by the fitting procedure. The value of E_0 for the larger PbS dots ($d \approx 3.8$ nm) is very close to the value of the gap observed at low temperature in agreement with the absence of the zero Kelvin renormalization observed in the isotopic studies in bulk PbS and attributed to the perfect cancelation of the energy shift originating from coupling to ‘Pb-’ and ‘S-like’ vibrations [33]. The more rapid decoupling to the low frequency phonons for smaller diameter PbS dots leads to a perfect cancelation of the overall energy shift with temperature for the smallest diameter PbS quantum dots, but the E_0 values obtained are slightly larger than the value of the band gap observed at low temperature, suggesting some band gap renormalization occurring at zero Kelvin.

In order to probe whether our assumption of selecting the phonon frequencies from the bulk density of states is correct, we have calculated the phonon spectra of PbS clusters for 3 different average diameter (5.2 Å, 8.2 Å and 10.0 Å). The clusters were constructed by taking the optimized bulk cell from Ref. [35] and drawing the predefined radii, such that we can keep a ratio as close as possible to the 50/50 stoichiometry ratio and keep a minimal possible number of unsatisfied surface atoms. No further optimization was performed to allow a direct comparison with the bulk system. Due to the computational cost originating from the large number of atoms, we have performed our total energy calculations within the projector-augmented wave (PAW) [36,37] method as implemented in the Vienna *ab initio* simulation package (VASP) [38–41]. Plane waves up to an energy cutoff of 350 eV were employed in order to achieve highly converged results and an accurate description of the dynamical properties. The exchange correlation energy is described within the GGA in the PBE [42,43] prescription. As it can be observed in Fig. 2, at small cluster sizes,

Table 1Parameters E_0 , E_1 , and E_2 used in the fitting procedures for PbS quantum dots shown in Fig. 1 and PbSe quantum dots shown in Fig. 2, respectively.

d (nm)	3.8		3.2		2.8
<i>PbS</i>					
E_0 (eV)	1.084		1.274		1.493
E_1 (meV)	4.1		2.5		1.0
E_2 (meV)	5.5		3.9		3.1
d (nm)	5.1	4.3	3.8	3.2	2.3
<i>PbSe</i>					
E_0 (eV)	0.833	0.967	1.077	1.243	1.656
E_1 (meV)	9.0	7.2	5.8	4.8	0
E_2 (meV)	14.7	13.0	12.1	10.4	7.1

**Fig. 2.** (Color online) Vibrational density of states for three different cluster sizes, 5.2 Å black dotted-dashed, 8.2 Å red dotted, 10.0 Å green dashed and PbS rocksalt bulk structure is in continuous blue line.

the vibrations are quite localized and little dispersion is noted, as it is expected for quasi molecular systems. As the system size increases, the vibrational spectra become broader and start to look quite similar to the bulk. In particular, we observe a rapid convergence of the low energy phonons resembling the bulk spectra, whereas the higher energy phonons show a slow convergence from 5.2 Å up to 10.0 Å radii. Finally, it should be pointed out the smallest quantum dot radius used in the experiment corresponds to 11.5 Å (2.3 nm diameter), therefore selecting the frequencies of the average phonons from the bulk density of states is permissible.

In Fig. 3(a) several representative absorption spectra of the 1s exciton state in PbSe quantum dots at different temperatures are shown. They are typical of all the quantum dots studied. In addition to the energy shift with temperature, a substantial reduction in broadening with decreasing temperature is observed, despite the large inhomogeneous linewidth due to the size distribution of the quantum dots. The same fitting procedure was used to reproduce the energy shifts of the band gap with temperature for PbSe quantum dots shown in Fig. 3(b–f). The average phonon frequencies obtained from the theoretical calculations and used in the fitting were $f_1 = 50 \text{ cm}^{-1}$ (6.06 meV) and $f_2 = 125 \text{ cm}^{-1}$ (15.5 meV) for PbSe [35]. The same trend was obtained for the E_1 and E_2 coefficients as in the case of PbS quantum dots, where both coefficients decrease with decreasing quantum dots size, but E_1 decreases more rapidly. For sufficiently small quantum dot diameters coupling to higher frequency vibrations dominates leading to a sign switch of the energy shift of the band gap with temperature. It appears that the effect of one oscillator which dominates in bulk and leads to the reversed

behavior of the band gap with temperature is overcome by the contribution of the other as the size of the quantum dot is reduced.

The confinement of phonons can lead to small shifts of their frequencies and the appearance of surface modes in colloidal quantum dots [44]. The effect of phonon confinement has been studied thoroughly theoretically and experimentally using Raman scattering starting in superlattices [45–50]. The effects of acoustic phonon folding, interface modes, and LO and TO phonon confinement on the Raman scattering spectra are described in detail in Ref. [51]. In quantum dots the phonon confinement effect on Raman scattering spectra due to Fröhlich interactions was modeled early on and calculated for CdS and CdSe quantum dots [44,52–56]. A detailed review of the effect of phonon confinement on the Raman scattering of nanostructures, including the theoretical models proposed, is provided in Ref. [57]. Experimentally, peak position shifts, broadening, and asymmetries in the Raman scattering spectra were observed [58]. Early work on the phonon properties of PbS quantum dots provided important insights into the electron–phonon interactions [59–61]. Infrared absorption spectra taken, which were independent of temperature between 15 K and 300 K. Two main dominant absorption peaks were observed at $\sim 90 \text{ cm}^{-1}$ and at $\sim 275 \text{ cm}^{-1}$, respectively.

In addition to our calculations, an atomistic potential model was used to study the phonon structure of GaP quantum dots [62]. These calculations concluded that depending on the spatial localization, the phonon modes in GaP quantum dots are either ‘bulk-like’ or ‘surface-like’. The modes that are localized within the interior of the GaP dot were found to have a clear bulk parentage in terms of their projection onto the bulk-phonon states. Therefore could be approximated by a single band at a single wave vector of the bulk phonon dispersion, whereas surface-like modes were found to be localized at the periphery of the dot and their eigenvectors were superpositions of many bulk phonon states from different bands and different points of the Brillouin zone. The calculations were performed for GaP quantum dots with diameter size in the range between $\sim 4.3 \text{ nm}$ and $\sim 2.2 \text{ nm}$. The calculated phonon density of states for GaP quantum dots differs somewhat from bulk for the smallest diameter and becomes similar to the bulk for larger diameters. Furthermore, phonon modes appear in the region where there are no bulk modes, which were thought to be localized on the dot surface. The peak intensities of these surface-like modes decrease significantly relative to the bulk-like modes with increasing dot size. Small shifts up or down in frequency were also observed for selected modes, where specific phonon modes showed a more dramatic shift. A microscopic lattice dynamical model has also been used to study the phonon modes of germanium quantum dots in the diameter range of interest here [63]. The phonon density of states showed a similar behavior to the GaP dots, where at lower diameters below $\sim 2 \text{ nm}$ discrete surface lattice modes appear. Low frequency spheroidal and torsional modes observed using Raman scattering were

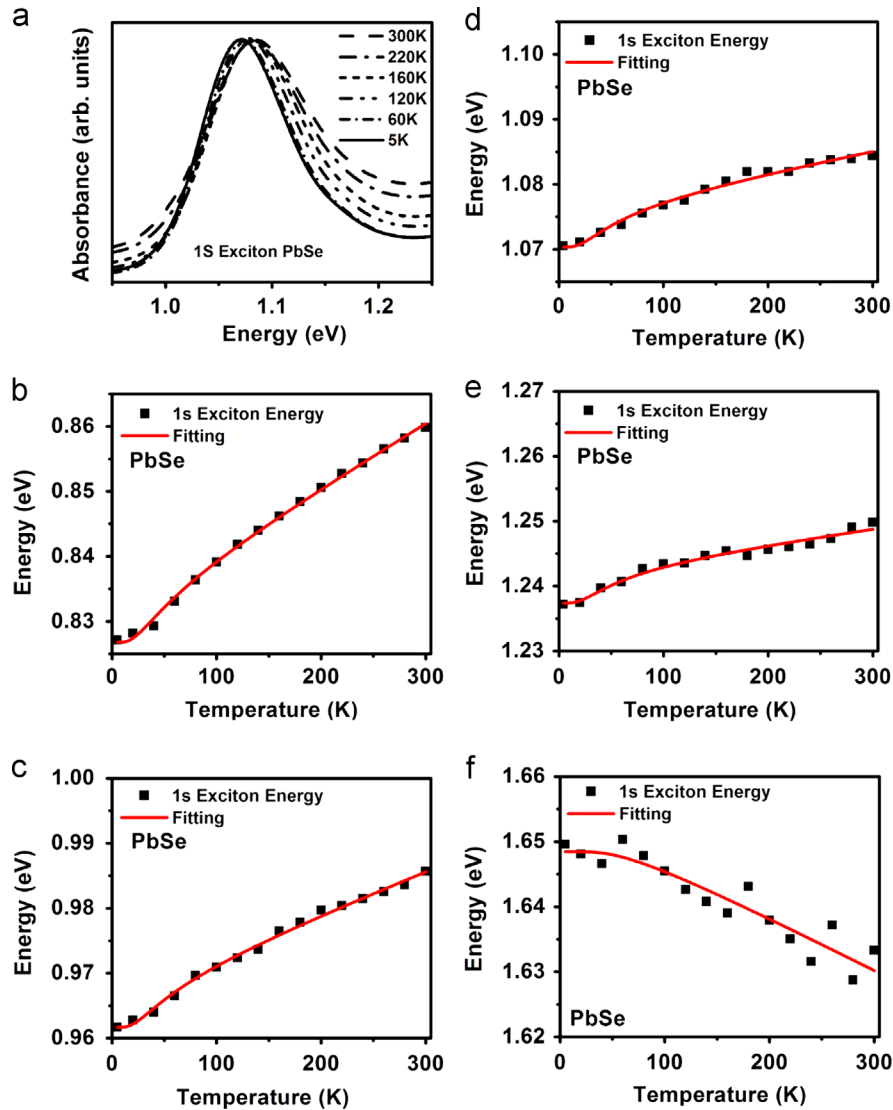


Fig. 3. (Color online) (a) The 1s exciton absorption peak of PbSe quantum dots for different temperatures. In addition to the energy shift with temperature, a reduction of the linewidth with decreasing temperature can be observed. (b)–(f) Temperature dependence of PbSe quantum dots for different diameters $d=5.1$ nm, $d=4.3$ nm, $d=3.8$ nm, $d=3.2$ nm, and $d=2.3$ nm, respectively. Squares are the experimental data whereas the red (grey) line is the fitting. (b)–(f) are plotted at the same (40 meV) energy axis for ease of comparison.

obtained for larger diameters. However, for smaller diameters the discrete surface lattice modes dominate the low frequency region. The phonon confinement appears to affect the phonon density of states of different materials similarly, but does not appear to have the same result on the temperature dependence of the band gap of other colloidal quantum dots of similar size.

4. Conclusions

In conclusion, we have carefully measured the temperature dependence of the 1s exciton energy of PbS and PbSe quantum dots for different diameter sizes. We observe a decrease of the 1s exciton linewidth with decreasing temperature despite the significant inhomogeneous broadening, which indicates large phonon broadening of the homogeneous linewidth. The 1s exciton energy shifts with temperature according to the band gap of the material. For larger diameter PbS and PbSe quantum the energy shift of the band gap decreases with decreasing temperature as observed in the corresponding bulk material. However, as the diameter size decreases, the energy shift of the band gap can be completely vanish or even switch sign, leading to a increase of the

band gap with decreasing temperature as observed in the vast majority of semiconductor materials. We used a simple two oscillator model extensively employed in the literature to model the band gap shift with temperature of bulk semiconductors. The average phonon frequencies were obtained from *ab initio* calculations of the phonon density of states of PbS and PbSe. *Ab initio* calculations of the phonon density of states for different crystal radii between 5.2 Å and 10 Å reveal a more rapid convergence of the low energy phonons and a slower convergence of the higher energy phonons. However, already at 10 Å radius the phonon density of states has converged and resembles the bulk phonon spectra. Using the two oscillator model, the coupling to predominant average phonons, low frequency ‘Pb-like’ and high frequency ‘S-’ or ‘Se-like’, respectively, was varied and reproduced well the energy shift of the band gap with temperature. Therefore, the band gap energy shift of PbS and PbSe quantum dots is thought to be predominantly a result of electron–phonon interactions. Since both, the reversed temperature dependence of the band gap in the bulk and the strong size dependence of the band gap shift in quantum dots are specific to lead chalcogenides, we conclude that the effects are most likely related. It is possible that CuCl or CuBr quantum dots of very small diameters, comparable to the

diameters studied here, could show very similar behavior. In the case of quantum dots, the reduction in size leads to a systematic decrease of the coefficients E_1 and E_2 . The interplay between the contributions described by two oscillators leads to a perfect cancelation or even switch in sign of the energy shift of the band gap with temperature. Since the origin of the increase of the band gap with increasing temperature in the bulk parent compounds is not entirely understood, it is difficult to conclude on the origin of such contributions. However, the likely explanation is the interplay between the electron–phonon renormalization and thermal expansion having opposite effect on the band gap energy. They can be described by the two oscillator model since both of these terms have a similar dependence on the phonon population factors, the vibrational amplitudes, and the atomic masses. The coupling to low frequency ‘Pb-like’ and high frequency ‘S-’ or ‘Se-like’ phonons, respectively, and as a result their contribution to the thermal expansion and electron–phonon renormalization systematically vary, as the diameter of the quantum dot is changed.

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