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Ultrafast lattice dynamics in lead selenide quantum dot induced by laser excitation

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We directly monitored the lattice dynamics in PbSe quantum dots induced by laser excitation using ultrafast electron diffraction. The energy relaxation between the carriers and the lattice took place within 10 ps, showing no evidence of any significant phonon bottleneck effect. Meanwhile, the lattice dilation exhibited some unusual features that could not be explained by the available mechanisms of photon-induced acoustic vibrations in semiconductors alone. The heat transport between the QDs and the substrate deviates significantly from Fourier's Law, which opens questions about the heat transfer under nonequilibrium conditions in nanoscale materials.

Keywords: PbSe quantum dot, phonon bottleneck, ultrafast electron diffraction, lattice dynamics

Narrow band gap lead chalcogenide PbX (X = S, Se, and Te) quantum dots (QD) are photoactive in the near infrared region with very high photoluminescence quantum yields. Electron and hole Bohr radii in PbX QD are large (e.g. about 23 nm in PbSe), such that both carriers experience very strong confinement effects in sub-10 nm particles, providing an additional channel to shape their physical properties by adjusting their sizes. Because of these unique features, PbX QDs pose great potential for a variety of optoelectronic and thermoelectric applications. An in-depth understanding of the property-size dependence, in particular how quantum confinement affects the dynamics of carrier and lattice coupling in QDs is central to realize their potential applications.

Due to strong quantum confinement effects¹, the electronic density of states becomes so discrete that the energy difference between adjacent electronic states exceeds several optical phonon energies. This change in the electronic density of states has been predicted to reduce the carrier-phonon relaxation rate significantly because the carrier-phonon coupling becomes an inefficient multi-phonon process (phonon bottleneck). Consequently, other relaxation pathways such as carrier multiplication²⁻⁷ and Auger relaxation⁸⁻¹⁰ are enhanced and observed in PbSe or PbS QDs. These effects open a possible mean to exceed the Shockley-Queisser limit of single junction solar systems. However, to people's big surprise, the long predicted phonon bottleneck is largely missing in various types of QDs.¹¹ Several studies attempted to unravel this mystery by monitoring the intra-band carrier relaxation, yielding a carrier-phonon relaxation time of about several picoseconds (*ps*)^{12,13}, comparable or even smaller than that of bulk materials. In addition, several new possible mechanisms that can bypass the phonon bottleneck in QDs have been proposed.^{11,14} However, there are still many open questions regarding the carrier and phonon dynamics, and their mutual interactions.

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FIG. 1. (a) A typical DP of PbSe QDs and (b) the corresponding intensity profile after background subtraction. Inset: the intensity profile of (2,2,0) peak at before 0 ps (open circle) and 10 ps (open square). The solid curves are corresponding fittings by a Lorentz function. (c) A TEM image of PbSe QD film and (d) the corresponding particle size distribution obtained by analyzing a large number of such images.

So far, with abundant research focusing on carrier dynamics in PbX QDs, the efforts on directly monitoring lattice dynamics are still sparse.^{15–17} In many cases, the knowledge of lattice dynamics is still derived indirectly from the information of carrier relaxation, where different decay pathways are intertwined together, obscuring the establishment of a clear picture of carrier-phonon relaxation. In this paper, we demonstrate a method of probing the electron-phonon coupling through directly monitoring the lattice system with ultrafast electron diffraction (UED). In particular, we simultaneously trace the lattice temperature change, the lattice dilation, and the heat transport between QDs and the substrate as a function of time. We found that the energy relaxation between the carriers and the lattice took place in less than 10 ps, showing no strong evidence of a phonon bottleneck. Meanwhile, the dilation of the lattice showed some unusual features that couldn't be explained by the mechanisms of photon-induced acoustic phonons in semiconductors¹⁸. In addition, the heat transport between the QDs and the substrate significantly deviated from the prediction of Fourier's Law¹⁹, requiring the use of the Cattaneo formula instead.

The experiment was conducted on our third-generation femtosecond (*fs*) electron diffraction instrument²⁰ at 60 keV electron beam energy (Debroglie wavelength ~ 0.0487 angstrom ($\text{\AA}$)). To keep an overall temporal resolution less than 500 *fs*²¹, the average electron-beam intensity was set to contain less than 1000 electrons per pulse. The high quality PbSe QDs were synthesized and dip-coated onto 50 nm thick Si_3N_4 membranes.²² As shown in Fig1(c) and (d), a large portion of the Si_3N_4 film was covered by QDs whose average size and size distribution were determined to be 5.8 nm and 0.2 nm (standard deviation) respectively.

Fig.1 (a) shows a typical diffraction pattern (DP) of the QD sample taken by UED apparatus. After a radial average of the intensity and subtracting the diffuse scattering background that mostly comes from the Si_3N_4 membrane, several Bragg peaks corresponding to the PbSe Halite structure were visualized, as shown in Fig.1 (b). To obtain a quantitative analysis, each Bragg peak was fitted with either a Gaussian or Lorentzian line profile to determine its center position, intensity, and width.²³ The intensity of each peak is further normalized to that of (2,0,0) peak to eliminate any abnormal changes not induced by the

FIG. 2. Results of static heating measurements: (a) relative center position change of Bragg peaks. The blue solid curve is a linear fit. (b) DWF change as a function of temperature. The blue dotted curve is the linear fit and the red solid curve is the DWF of bulk PbSe material.

pump laser.

Static measurements were first conducted to determine the linear expansion coefficient and Debye-Waller factor (DWF) by placing the samples on a heating-cooling stage and taking DPs at different sample temperatures. Following sample heating, the center position of each Bragg peak shifted towards lower diffraction angle fairly linearly as a function of the sample temperature, as shown in Fig.2 (a). However, the obtained linear thermal expansion coefficient $((1.103 \pm 0.17) \times 10^{-5} K^{-1})$ is significantly smaller than the bulk value $(\sim 1.8 \times 10^{-5} K^{-1})$ ²⁴ around the same temperature range. Meanwhile, the intensity of each Bragg peak also dropped as sample temperature increases. The relation between the Bragg peak intensity (normalized to (2,0,0) peak) and the sample temperature can be written as²⁵:

$$\frac{I_{h,k,l}}{I_{2,0,0}} = \exp\left(\frac{-B(T)(h^2 + l^2 + k^2 - 2^2)}{2a^2}\right), \quad (1)$$

where h, k, l are the miller indices and a is the lattice constant. $B(T)$ is the DWF that can be written as a polynomial function of temperature²⁵:

$$B(T) = \alpha T + \beta T^2 + \dots \quad (2)$$

where the first term is the harmonic term and the second term is a small correction due to the quasiharmonic and isotropic anharmonic contributions. $B(T)$ of the PbSe QDs was evaluated according to Eq.1 and was found to be always smaller than the bulk value²⁶, as shown in Fig.2 (b). However, if the $B(T)$ data was fitted by a linear function, the slope was found to be $(4.20 \pm 0.6) \times 10^{-3} \text{\AA}^2 K^{-1}$, very close to the coefficient of the harmonic term $(\alpha = 4.15 \times 10^{-3} \text{\AA}^2 K^{-1})$ in Eq.2 for the bulk²⁶, which implies that both the quasiharmonic and isotropic anharmonic contributions were reduced in the QD sample. Since the quasiharmonic term is the correction due to thermal expansion, its reduction was linked to the observed reduction of thermal expansion in PbSe QDs. We speculated that the reduction of both linear expansion coefficient and DWF in PbSe QDs might be related to the restriction from the Si_3N_4 substrate whose thermal expansion coefficient was much smaller than the QDs. Meanwhile, factors such as the quality of the QDs, the size effect of the QD, and other physical properties may also affect these values. Therefore, it is critical to calibrate all the associated parameters *in situ* before conducting time-resolved experiments.

In the pump-probe experiment, the lattice dynamics was initiated with 800 nm, 50 fs laser pulses and recorded by capturing snapshots of DPs at various pump-probe delay times. The sample base temperature was set at 146 K and the laser fluence was fixed at $\sim 5 \mu J mm^{-2}$. Fig.3 (a) shows the DWF change as a function of delay time extracted from the transient Bragg peak intensity data according to Eq.1. The corresponding lattice temperature obtained according to the calibrated $B(T)$ curve from the static measurement is also given in the figure. Compared to the averaged lattice spacing change as a function of delay time (extracted from the center position of the Bragg peaks) plotted in Fig.3 (b), it can be seen that the lattice temperature initially increased within about 10 ps and then decreased back to the original value in about 40 ps. The maximum lattice temperature

FIG. 3. (a) The change of DWF (solid square) as a function of time. The solid line is the model fitting (see context for details). The asterisk line is a simulation of the evolution of carriers' excessive energy due to Auger relaxation. (b) Relative lattice spacing change (open circle) as a function of time. The dashed line is for guiding viewer's eyes which has no theoretical significance.

change was about 80 K corresponding to the energy of 48 absorbed photons per QD. This is about 80% of our estimation of photon absorption. The lattice spacing also showed an initial 6 ps increase followed by a decrease thereafter. However, it didn't return back to the original value, unlike the behavior observed for the lattice temperature change.

The observed ultrafast lattice dynamics are governed by the mutual interactions between the photon-excited carriers (electrons, holes and/or electron-hole pairs) and lattice subsystems.²⁷ Since the bandgap E_g of a 5.8 nm PbSe QD is about 0.8 eV, after absorbing 1.55 eV photons, the electrons are excited into the conduction band with about 0.75 eV excessive energy per electron-hole pairs. These carriers redistribute their energies among themselves by various carrier-carrier scattering process. Particularly, via Auger scattering^{8,9}, a portion of the electrons and holes recombine while transferring their energy to the remaining ones and exciting them into even higher energy states. Meanwhile, the carriers relax their energy to the lattice system by carrier-phonon scattering leading to an increase of the lattice temperature and a decrease of overall carrier energy. Both optical and acoustic phonons (OP and AP) can couple to carriers, while different phonon modes are also coupled to one another. In this situation, a phenomenological three temperature model (TTM)^{28,29} is usually used to describe the kinetics of energy interchange among participating subsystems. We modified this model in several aspects to suit the particular need of our data analysis. Since the electronic states of the QD are quite discrete, it is questionable that a uniform temperature can be established and govern the carrier-phonon coupling in such a short time-scale of a few ps. So instead of using temperature, we used excessive energy E_{ex} to characterize the carrier sub-system and also assumed that E_{ex} governs the carrier-phonon coupling. For the lattice system, we ignored the detailed dynamics of the carrier-OP and then OP-AP coupling, instead using only one effective rate to describe the energy flow from carriers to lattice. Actually, from the AP sub-system's point of view, the energy comes either directly from the carriers by carrier-AP coupling or indirectly from OP by carrier-OP and OP-AP coupling. In bulk semiconductors, it is generally believed that carrier-OP scattering is much faster than carrier-AP scattering; however, for QDs, both couplings become important^{11,30}. As in the TTM, the AP system can be characterized by a

temperature T_l , which also governs the heat transport between QD and the substrate. The spatial variation of T_l was ignored because the QDs were very small. Also, the substrate temperature T_s was assumed to remain constant during the entire process because the heat capacity of substrate was much larger than that of the QDs. Based on these assumptions, the ultrafast lattice dynamics can be represented by:

$$\frac{dE_{ex}}{dt} = \frac{AE_g V n_0^3}{(1 + 2An_0^2 t)^{1.5}} - \frac{E_{ex}}{\tau} + S(t) \quad (3)$$

$$C_p \frac{dT_l}{dt} = \frac{E_{ex}(t)}{\tau} + q \quad (4)$$

$$q = -\tau_R \frac{dq}{dt} - h(T_l - T_s) \quad (5)$$

where V is the volume of the QD, τ is the time constant that characterizes the carrier-phonon coupling, and $S(t)$ is the laser pumping term. Since the laser pulse is very short, a Dirac delta function is used to represent laser pumping: $S(t) = (1.55 - E_g)N\delta(t)$, where N is the number of absorbed photons, $n_0 = N/V$ is the initial density of excited carriers, C_p is the averaged heat capacity per QD,³¹ and q represents the energy flow between the QD and the substrate. The first term on the right hand of Eq.3 represents the Auger relaxation process which has been extensively studied by optical methods and $A = 5 \times 10^{-42} m^6 s^{-1}$ is the Auger constant³². Eq.5 is the Cattaneo equation¹⁹ with τ_R as the retarded time constant and h as the product of thermal contact conductance and contact area. We define $\tau_{heat} = C_p/h$ as the time constant of heat transport between the QD and the substrate.

To model the transient lattice temperature data, we further assume that the observed DWF change all comes from AP, because the DWF is inversely proportional to the square of the vibrational frequency and therefore the OP contribution was relatively small. We adjusted τ_R , τ , and τ_{heat} until the T_l curve gave a reasonable fit of our data as shown in Fig.3 (a). For comparison, the evolution of E_{ex} due to Auger relaxation is also plotted (converted to equivalent lattice temperature change). It can be seen that the Auger relaxation time is about 1 ps and is much shorter than all the other time constants. So from the lattice point of view, it serves as a second energy source following the laser pulse. τ is around 10 ps and is not significantly longer than the bulk value, showing no sign of any pronounced effect of phonon bottleneck. It is worth pointing out that the τ obtained in our experiment should be larger than the carrier-phonon relaxation time extracted from carrier's intraband transition measurements because many scatterings are needed in order to remarkably increase the lattice temperature. Thus, our observation is consistent with previous studies where a several ps relaxation time are observed^{12,13}. Several mechanisms have been proposed to explain the absence of the phonon bottleneck by considering surface states¹¹, polaronic effect^{33,34}, localization of carrier's wavefunction and nonadiabatical carrier-phonon coupling^{11,14,35}. Besides all these contributions, we believe that Auger relaxation also played an important role. Since the pumping fluence was very high in our experiments, the Auger relaxation is significantly enhanced, which tends to excite more carriers into higher energy states or even state continuum where the quantum confinement is not so important. As a result, carriers could very quickly relax energy to lattice before returning back to the discrete states.

Regarding the heat transport between the QDs and substrate, we found that the retarded term with $\tau_R = 10$ ps in the Cattaneo equation was very critical for the data fitting without which a significant deviation from our data will exist. This seems to imply that under high pumping fluence, a non-thermal-far-from-equilibrium condition is established in QDs, where Fourier's Law doesn't hold. However, like in many other non-thermal energy transfer cases in nanostructures, the Cattaneo equation is phenomenological and the rigid physical meaning of the τ_R is still need to be defined.¹⁹

The transient lattice spacing change as shown in Fig.3 (b) raised some interesting points. In general, the dilation of the lattice can be driven either by carriers and/or phonons and is usually accompanied by a coherent vibration initially^{16,36}. The total stress can be expressed

by¹⁸:

$$\sigma = \sigma_{TE} + \sigma_{DP} + \sigma_{other} \quad (6)$$

where σ_{TE} is the stress from phonons due to thermal elasticity, σ_{DP} is the stress from carriers due to deformation potential, and σ_{other} accounts for all other contributions including inverse piezoelectricity, electrostriction, charging, surface dipolar fields and so on. Although σ_{TE} of PbSe is *tensile*³⁷, it was unable to expand the lattice faster than T_l in the absence of a coherent vibration³⁶. So the observed lattice spacing change clearly indicates the contribution of σ_{DP} and σ_{other} . Moreover, Based on the pressure derivative of the energy gap in PbSe QDs³⁸, when carriers relax to the bottom of the conduction band, σ_{DP} is *compressive* that can drive the lattice to *shrink* about 0.08% per carrier. As a comparison, σ_{TE} could only expand the lattice about 0.09% for $\Delta T_l = 80\text{ K}$. However, we didn't see any trend of lattice shrinking although the initial number of excited carriers are very high. We believe that this is another evidence of Auger relaxation that keeps exciting the carriers to higher energy states which may have an overall tensile stress. After about 40 ps when both lattice temperature and excited carriers return back to the original condition before time-zero, there is still about 0.05 % change remaining. So we speculate that σ_{other} must be nonzero and tensile, even though PbSe shows no significant piezoelectricity nor electrostriction effect under normal conditions. However, under a high-pumping-fluence, we speculated that charges may be built and trapped in the interface which can establish local fields¹⁶ to expand the QD. Future studies will provide more insights into the origin of lattice spacing change.

In summary, we directly monitored the photoexcited ultrafast lattice dynamics of PbSe QDs using UED. A phenomenological model was presented to explain the observed lattice temperature change as a function of delay time. We found that the energy relaxation between the carriers and lattice took place within 10 ps showing no strong evidence of a phonon bottleneck. Such a process implies that the carrier's Auger relaxation might have played an important role by exciting more carriers to high energy states where the phonon bottleneck is bypassed. In addition, the lattice dilation might be driven by extra tensile stress as well as the thermal stress from the lattice and the stress from the carrier's lowest energy state. The charging of QD induced by photoexcitation could also be one important factor. Furthermore, the heat transport between the QD and substrate seems to follow Cattaneo equation rather than Fourier's Law, which is consistent with previous work on the non-equilibrium nanoscale heat transport.²⁹ These observations provide experimental framework for the further theoretical investigations to understand the ultrafast lattice dynamics of QDs under non-thermal equilibrium conditions.

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Peak position change