

## Evidence for Barrierless Auger Recombination in PbSe Nanocrystals: A Pressure-Dependent Study of Transient Optical Absorption

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We report rates of Auger recombination (AR) in zero-dimensional (0D) PbSe nanocrystals as a function of energy gap ( $E_g$ ) by using applied hydrostatic pressure to controllably shift  $E_g$  according to the bulk deformation potential. Our studies reveal that the rate of AR in nanocrystals is insensitive to energy gap, which is in contrast with bulk semiconductors where this rate shows exponential dependence on  $E_g$ . These measurements represent the first direct experimental evidence that AR in 0D nanomaterials is barrierless, in distinction from bulk semiconductors.

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Auger recombination (AR) is a technologically important, many-body carrier recombination process that competes with gain in optical amplifiers [1] and reduces the brightness of light emitting diodes at high current [2]. In AR between uncorrelated carriers, one electron-hole ( $e$ - $h$ ) pair nonradiatively recombines and transfers its energy to a third carrier (an electron or a hole), resulting in a net loss in the total number of excited carriers. In bulk semiconductors, this process exhibits an energy barrier that arises from the requirements of energy and translational momentum ( $p$ ) conservation. In short, the third carrier must gain the energy and momentum of the recombined  $e$ - $h$  pair. Thus, only combinations of carriers with sufficient initial energy can undergo AR [see Figs. 1(a) and 1(b); one carrier is a spectator]. The energy threshold ( $E_A$ ) for activating AR is directly proportional to energy gap  $E_g$  since  $E_g$  dictates the momentum acquired by the third carrier. Thus, the AR rate ( $k_{AR}$ ) is exponentially dependent upon  $E_g$  as  $k_{AR} \propto \exp[-\gamma E_g/kT]$ , where  $T$  is temperature,  $\gamma$  is a constant dependent on the electronic structure, and  $k$  is the Boltzmann constant [1,3]. An activation threshold is observed for bulk semiconductors in temperature-dependent studies of AR rates [3] and is implicit from the ca. 5-orders-of-magnitude per 1-eV variation that is observed in AR rates for semiconductors as a function of  $E_g$  [4].

AR also plays an important role in quantum-confined semiconductor nanocrystals (NCs). As established experimentally [5–13], this process dominates carrier population dynamics when multiple  $e$ - $h$  pairs are excited per NC, and hence, it represents a major carrier-loss mechanism in potential NC applications such as lasing [14] and solar cells enhanced by carrier multiplication [9,15]. Previous experimental [5,8,11–13] and theoretical studies [16,17] indicate that, in zero-dimensional (0D) NCs, AR is a three-particle decay process, which is a result of the fact that Coulombic  $e$ - $h$  interaction energies in NCs are much smaller than carrier confinement energies [18], and hence, electron and hole motions in these NCs are not correlated.

The constraints imposed upon AR by momentum conservation in the bulk are expected to be relaxed in NCs [17,19,20]. Carriers contained within NCs reside in discrete, atomiclike levels [see Fig. 1(c)], which are classified according to angular momentum ( $M$ ) but not translational momentum [21]. Thus, it is expected that AR in NCs must conserve total carrier energy and angular momentum but not translational momentum. In this case AR should occur

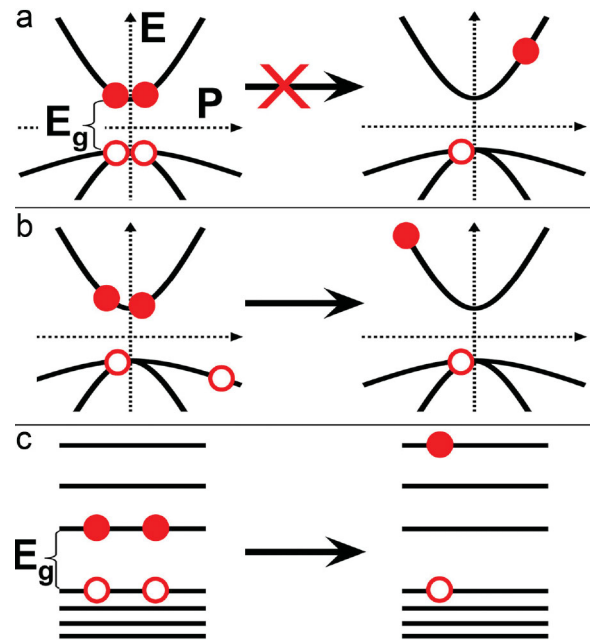


FIG. 1 (color). (a) Low-energy carriers (solid and empty symbols are electrons and holes, respectively) in a bulk semiconductor with energy gap  $E_g$  cannot undergo AR due to requirements that energy ( $E$ ) and momentum ( $p$ ) are conserved simultaneously. (b) Higher energy carriers can undergo AR in a bulk semiconductor. (c) Low-energy carriers in a semiconductor NC can undergo AR due to the discrete character of the energy levels, which results in relaxation of translational momentum conservation.

without an energetic barrier because carrier energy and  $M$  are not directly related, and hence, the carrier that is reexcited can easily access an energy-conserving state with an appropriate value of  $M$  [17,20]. This difference from bulk has several ramifications. The lack of a barrier to AR in NCs means that (i) low-energy  $e$ - $h$  pairs are available for AR whereas in the bulk they are not [compare Figs. 1(a) and 1(c)], (ii) temperature does not influence AR rates, (iii) NC size (which defines Coulomb coupling) and wave function overlap alone determine AR rates rather than the energy gap, and (iv) the inverse-AR process of impact ionization [1] may also be barrierless. Despite the ubiquity of AR in NC materials, direct experimental evidence in support or opposition to this concept of barrierless AR in NCs is still notably absent from the literature.

One significant problem in verifying barrierless AR in NCs is the difficulty in decoupling the effects of NC size and energy gap on AR rates. For two  $e$ - $h$  pairs, experimentally measured AR rates exhibit a cubic dependence on NC radius,  $R$  [5,9,11]. This size dependence can arise from multiple factors including changes in the effective carrier concentration (scales as  $R^{-3}$ ), the strength of Coulomb coupling (proportional to  $R^{-1}$ ), the density of the final states for the reexcited carrier, and potentially, the size-dependent energy gap, which in the particle-in-a-box model changes as  $R^{-2}$ .

In this Letter, we use pressure to tune the NC energy gap via bulk deformation potential without causing significant changes in NC size. Because deformation potentials and bulk moduli of many semiconductors are large, significant shifts in energy can be achieved with only small changes in NC volume, and often without moving the crystal through a phase transition [22]. Specifically, we use transient absorption (TA) to investigate AR of two  $e$ - $h$  pairs in PbSe NCs contained within a diamond anvil cell (DAC), which is used to isostatically and reversibly apply large pressures to the NCs in solution. Because of a large Bohr radius (46 nm), sub-10 nm PbSe NCs are ideally suited to the investigation of an activation barrier since both carriers are in the regime of strong quantum confinement [23]. We start by confirming the relatively small NC-volume change and constancy of crystal phase for a range of pressures using x-ray diffraction (XRD). We find that the AR rate is not dependent upon  $E_g$ , in accordance with the concept of barrierless AR. Finally, we observe a slight reduction in the two-pair lifetime with pressure that correlates with the concomitant slight reduction in NC volume.

PbSe NC samples were synthesized [24,25], dissolved in ethylcyclohexane (which does not crystallize under pressure), and loaded into a DAC. A ruby chip was also placed in the DAC for determination of applied pressure via ruby  $R1$  fluorescence using  $P(\text{GPa}) = \Delta\lambda_{R1}(\text{nm}) \times 2.740$  [26]. Room temperature absorption spectra, XRD, and TA dynamics were then measured as a function of pressure. TA measurements were performed using previously reported

methods [9]. For each pressure, the TA probe wavelength was tuned to the pressure-dependent, lowest-energy 1S absorption maximum (corresponding to  $E_g$ ) as determined by absorption spectroscopy.

Previously, AR rates have been measured using TA for quantum-confined semiconductor NCs of several compositions [5–13,27]. Two  $e$ - $h$  pair lifetime ( $\tau_{\text{AR}} = 1/k_{\text{AR}}$ ) has been found to scale linearly with NC volume for a variety of materials including CdSe [5], PbSe [9], and InAs [11]. Two  $e$ - $h$  pair AR yields a distinct, tens- to hundreds-of-picosecond relaxation component in TA dynamics that is easily distinguishable from the long-lived single  $e$ - $h$  pair dynamics [6,28]. It is noteworthy that the two  $e$ - $h$  pair lifetimes for different materials are comparable within a factor of 3 for a given NC volume, even for large ( $\sim 1$  eV) differences in  $E_g$  [5,9,11], suggestive of significant differences from AR in the bulk. Investigation of the AR process as a function of  $E_g$  in a single NC material system is complicated by the inexorable link between volume and  $E_g$ , which renders independent assessment of the influence of each on AR rate unfeasible. The presence or absence of an AR energy barrier can only be established by separating these normally codependent variables, which is accomplished here using pressure.

Hydrostatic pressure has been used to study NC materials in the context of crystal phase transitions [22] and optical absorption [29,30]. We suggest that pressure also represents a powerful, relatively untapped tool for the study of carrier dynamics as a function of  $E_g$  separated from effects of NC size. Moreover, manipulation of  $E_g$  via control over NC size allows many other properties of the material to vary significantly, including extent or effectiveness of surface passivation, detailed chemical composition (the exact stoichiometry of binary compound NCs can vary with details of synthetic method), surface faceting, shape, etc. Through application of pressure, we can control  $E_g$ , according to the bulk deformation potential, with very small changes in NC volume while leaving shape and chemical properties fixed (as inferred from the observed reversibility).

Figure 2(a) shows pressure-dependent XRD patterns for a PbSe NC sample (1.5-nm radius at ambient pressure). The diffraction peaks are broadened relative to bulk-phase PbSe (shown at ambient pressure as filled peaks) due to the smaller average NC domain size. Nonetheless, the expected rocksalt cubic pattern is readily apparent. The shift of each peak towards larger  $2\theta$  (smaller  $d$  spacing) was used to determine the unit-cell change, and hence, NC volume [Fig. 2(b)]. For samples of radii ranging from 1.5 to 6 nm, the NC volume decreases by up to  $\sim 10\%$  over the pressure range used in AR studies (up to 7 GPa). The experimentally determined compression is smaller than that predicted by the bulk modulus, which may be a reflection of the increased influence of surface atoms due to the high surface-to-volume ratios in NCs. Most impor-

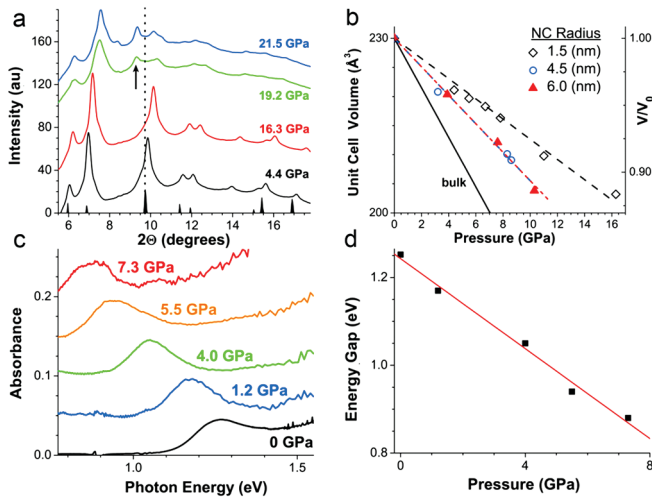


FIG. 2 (color). (a) X-ray diffraction (using  $0.3678 \text{ \AA}$  x rays) as a function of applied hydrostatic pressure for 1.5-nm radius PbSe NCs. XRD of bulk PbSe at ambient pressure is shown as the filled spectrum. These measurements indicate that this sample undergoes a phase transition between 16 and 19 GPa. (b) Cell volume as a function of applied pressure for three PbSe NC samples. The solid black line corresponds to bulk-phase PbSe. (c) Absorption spectra of 1.5-nm radius PbSe NCs as a function of applied pressure show an energy gap shift of  $-50.7 \text{ meV/GPa}$ . (d) The pressure dependence of  $E_g$  extracted from (c).

tantly, the onset of a change in crystal phase was not observed until pressures well in excess of those probed spectroscopically. For the nominally 1.5-nm NC sample, new diffraction peaks are observed at pressures  $>19 \text{ GPa}$ , likely a sign of a nascent, but incomplete, transition to GeS- and/or CsI-like crystal structures [31].

The pressure dependence of  $E_g$  for a 1.5-nm radius PbSe NC sample (size measured by transmission electron microscopy) was determined by optical absorption [Fig. 2(c)]. The band-edge 1S absorption feature systematically shifts to lower energy with applied pressure as observed previously [30]. The rate of this shift of  $-51.3 \text{ meV/GPa}$  [Fig. 2(d)] is comparable to the bulk deformation potential of  $-59.5 \text{ meV/GPa}$  [30]. These results demonstrate the considerable tunability of  $E_g$  with applied pressure. In bulk semiconductors, such changes in  $E_g$  (at 7.3 GPa,  $\Delta E_g = -370 \text{ meV}$ ) would be expected to increase the AR rate by ca. 3 orders of magnitude.

Figure 3(a) shows TA measurements performed on PbSe NCs contained in a DAC using a range of pump intensities (here for a pressure of 4 GPa, a probe energy of 1.05 eV, and for a sample of 1.5-nm radius PbSe NCs). For all measurements, a transient bleach of absorption is observed ( $-\Delta\alpha$ ) that is ascribed to state filling of the band-edge levels. Low pump-intensity measurements reveal that bleach recovery dynamics for a single  $e-h$  pair per photo-excited NC are flat on the subnanosecond time scale

(which indicates that processes such as fast carrier trapping are not prevalent). As pump intensity is increased such that more than one  $e-h$  pair per NC is produced in some NCs, a faster relaxation component is observed in the 1S bleach dynamics. Such pump-intensity dependent relaxation dynamics are attributed to AR of two  $e-h$  pairs [5–13], as radiative recombination of two  $e-h$  pairs is expected to be 3 orders of magnitude slower based upon the long-lived single  $e-h$  pair [6,28].

TA measurements performed on the 1.5-nm radius PbSe NCs at several applied pressures are shown in Fig. 3(b). The pump intensity was held constant and sufficiently high such that the regime of two  $e-h$  pair AR could be observed. Ratios of bleach amplitudes for different pressures at short pump-probe delay relative to long delay time were held constant for each measurement. We observe that the two  $e-h$  pair lifetime does not dramatically change as the  $E_g$  of

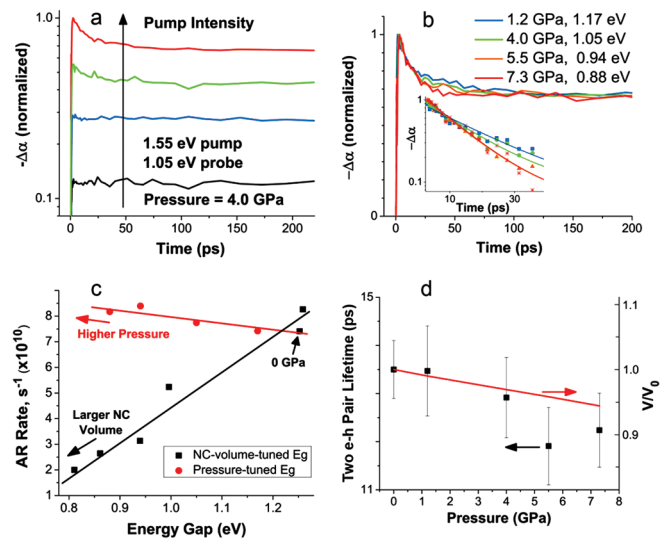


FIG. 3 (color). (a) TA as a function of pump intensity under applied pressure (4 GPa) for pump pulse fluences from 0.3 to  $2.3 \times 10^{15} \text{ photons/cm}^2$ . At low pump intensity, single  $e-h$  pair dynamics are observed, which are flat on the subnanosecond time scale. At higher intensity, a faster relaxation process is observed that is attributed to AR between uncorrelated carriers. (b) AR measurements of 1.5-nm radius NCs as a function of indicated pressure and  $E_g$  exhibit very slight variation. The measurement at ambient pressure is not shown for clarity, but is largely indistinguishable from measurements at 1.2 GPa. The inset shows extracted two  $e-h$  pair AR dynamics [5]. (c) Comparison of AR rates vs NC energy gap for NC-volume control at ambient pressure using several NC samples (black squares) or pressure tuning of a single NC sample (red circles). The black square labeled “0 GPa” denotes the ambient pressure NC sample. (d) Two  $e-h$  pair lifetime (left axis) and relative change in NC volume (right axis) as a function of applied pressure indicates that changes in the two  $e-h$  pair lifetime with pressure can be explained simply by the decrease in NC volume under compression. The red line corresponds to the measured relative change in NC volume from Fig. 2(b).



the NC sample is shifted to lower energy. The extracted two  $e$ - $h$  pair lifetimes (following subtraction of the long-lived single  $e$ - $h$  pair dynamics), plotted in the inset of Fig. 3(b), show that a small (up to  $\sim 10\%$ ) but systematic decrease in two  $e$ - $h$  pair lifetime occurs with increasing pressure (i.e., decreasing  $E_g$ ).

From these TA observations, two important conclusions can be drawn. The first is that AR rates in these NCs do not show a bulklike dependence on  $E_g$ . Though the AR rates measured using applied pressure do increase with decreasing energy gap, the change is small, and clearly not exponential [Fig. 3(c), red circles]. A comparison of the change in AR rate with pressure-induced  $E_g$  shift relative to that with size-induced shift [Fig. 3(c), black squares] reveals a stark contrast in magnitude and direction that leads to our second conclusion: AR rate in NCs depends primarily upon NC volume. While the trend is unmistakable in the size-controlled study [Fig. 3(c), black squares], support for this statement from the pressure-controlled data requires closer inspection. In Fig. 3(d), the two  $e$ - $h$  pair lifetime is shown as a function not of  $E_g$ , but of pressure, along with the measured relative change in NC volume. When plotted in this manner, the relation becomes clear: the two  $e$ - $h$  pair lifetime decreases (AR rate increases) in direct proportion to the decrease in NC volume. In fact, when we consider the pressure-induced change in NC volume (by XRD), the measured decrease in the two  $e$ - $h$  pair lifetime with pressure actually scales closely with the decrease in NC volume as predicted by the size-controlled study (albeit over a much smaller range of size).

Overall, we find that AR rates in strongly quantum-confined NCs are principally governed by NC dimensions. Specifically, for the small changes in NC volume and large changes in  $E_g$  that are accessible with pressure, two  $e$ - $h$  pair AR lifetime changes little indicating that  $E_g$  is largely irrelevant in quantum-confined AR. Thus, AR in NCs does not appear to exhibit an energetic barrier in stark contrast to bulk semiconductors. In future work, we will aim to resolve the question of an energetic barrier to AR in the cases of intermediate and weak quantum confinement where one or more carriers exhibit a quasicontinuous, bulklike density of states.

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- [1] B. K. Ridley, *Quantum Processes in Semiconductors* (Clarendon Press, Oxford, 1982).
- [2] N. K. Dutta and R. J. Nelson, *IEEE J. Quantum Electron.* **18**, 375 (1982).
- [3] A. R. Beattie and P. T. Landsberg, *Proc. R. Soc. A* **249**, 16 (1959).
- [4] G. W. Charache *et al.*, *J. Appl. Phys.* **85**, 2247 (1999).
- [5] V. I. Klimov *et al.*, *Science* **287**, 1011 (2000).
- [6] B. L. Wehrenberg *et al.*, *J. Phys. Chem. B* **106**, 10634 (2002).
- [7] R. J. Ellingson *et al.*, *J. Phys. Chem. B* **106**, 7758 (2002).
- [8] H. Htoon *et al.*, *Phys. Rev. Lett.* **91**, 227401 (2003).
- [9] R. D. Schaller and V. I. Klimov, *Phys. Rev. Lett.* **92**, 186601 (2004).
- [10] M. C. Beard *et al.*, *Nano Lett.* **7**, 2506 (2007).
- [11] R. D. Schaller *et al.*, *Nano Lett.* **7**, 3469 (2007).
- [12] V. I. Klimov *et al.*, *Phys. Rev. B* **77**, 195324 (2008).
- [13] E. Istrate *et al.*, *J. Phys. Chem. B* **112**, 2757 (2008).
- [14] V. I. Klimov *et al.*, *Science* **290**, 314 (2000).
- [15] R. Ellingson *et al.*, *Nano Lett.* **5**, 865 (2005).
- [16] A. Franceschetti *et al.*, *Nano Lett.* **6**, 2191 (2006).
- [17] L. W. Wang *et al.*, *Phys. Rev. Lett.* **91**, 056404 (2003).
- [18] Electron-hole-pair binding energy in bulk PbSe is  $\sim 0.6$  meV, while confinement energies in the NCs under investigation are  $\sim 1$  eV.
- [19] D. I. Chepic *et al.*, *J. Lumin.* **47**, 113 (1990).
- [20] V. A. Kharchenko and M. Rosen, *J. Lumin.* **70**, 158 (1996).
- [21] D. J. Norris *et al.*, *Phys. Rev. Lett.* **72**, 2612 (1994).
- [22] S. H. Tolbert and A. P. Alivisatos, *Science* **265**, 373 (1994).
- [23] F. W. Wise, *Acc. Chem. Res.* **33**, 773 (2000).
- [24] C. B. Murray *et al.*, *IBM J. Res. Dev.* **45**, 47 (2001).
- [25] J. M. Pietryga *et al.*, *J. Am. Chem. Soc.* **126**, 11752 (2004).
- [26] G. J. Piermarini *et al.*, *J. Appl. Phys.* **46**, 2774 (1975).
- [27] A. Pandey and P. Guyot-Sionnest, *J. Chem. Phys.* **127**, 111104 (2007).
- [28] H. Du *et al.*, *Nano Lett.* **2**, 1321 (2002).
- [29] S. H. Tolbert *et al.*, *Phys. Rev. Lett.* **73**, 3266 (1994).
- [30] K. K. Zhuravlev *et al.*, *Appl. Phys. Lett.* **90**, 043110 (2007).
- [31] J. Maclean *et al.*, *Nucl. Instrum. Methods Phys. Res., Sect. B* **97**, 354 (1995).