Temperature and size-dependent suppression of Auger recombination in quantum-confined lead salt nanowires

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Auger recombination (AR) is a nonradiative process, in which the electron-hole recombination energy is transferred to a third charge carrier exciting it to a higher-energy state. In bulk semiconductors, AR is inefficient because of constraints imposed by energy and translational-momentum conservation. But due to relaxation of translation-momentum conservation, the efficiency of Auger-like processes is greatly enhanced in quantum-confined nanocrystals (NCs), where AR plays a central role in carrier relaxation.

Effectively one-dimensional nanowires (NWs) occupy an intermediate position between zero-dimensional NCs and bulk materials. In sufficiently long NWs of the length L essentially exceeding the NW radius R, a longitudinal motion of charge carriers along the NW axis is free, while a transverse motion in the plane perpendicular to the NW axis is spatially quantized. The electronic structure of quantum-confined NWs is composed of subbands of the longitudinal motion with a wave vector k, which are also characterized by a spatially quantized wave vector of the transverse motion p. Since electronic transitions between subbands with different p are not forbidden by longitudinal wave vector conservation, quantum confinement in NWs is expected to result in enhancement of Auger effect compared with bulk parent materials.

In particular, Auger decay of the ground bieexciton state, which is forbidden in the bulk by energy and translation-momentum conservation, is expected to be allowed in quantum-confined NWs.

A strong coupling between the conduction and the valence bands in lead salt materials results in significant corrections to the electronic structures of NCs and NWs computed in the framework of “particle-in-a-box” model accounting for the interband coupling. However, in the case of NCs, these corrections are mainly quantitative and do not lead to new qualitative physical results. In particular, no essential difference is observed in size dependence of AR in narrow-gap NCs and NCs made of wide-gap materials, in which contribution of the interband coupling is relatively small.

But a situation is essentially changed for NWs with a strong interband coupling. In contrast to the case of NCs, the interband coupling in NWs significantly lifts degeneration of low-energy single-particle states of the transverse electron motion resulting in specific selection rules for Auger-like processes. That in its turn leads to qualitative changes in temperature and size behavior of AR compared with those in NCs and bulk materials.

In this paper, employing results of our recent studies of the electronic structure of quantum-confined lead salt NWs, we show that, in sharp contrast to the case of NCs, AR of the ground bieexciton state is strongly suppressed, and only excited bieexciton states, which are partially populated at finite temperature, contribute to Auger decay of bieexcitons. Thus, the total rate of bieexciton AR is given by the sum of the rates of excited bieexciton states with conventional weight factors, which determine their population at finite temperature T:

\[ W(T, R) = \sum_n W_n(R)e^{-\Delta E_n(R)/T}. \]

Here, size-dependent \( \Delta E_n \) is the energy difference between n-th excited bieexciton state with the AR rate \( W_n \) and the ground bieexciton state. Analytical and numerical computations show that, again in contrast to the case of NCs, size dependence of matrix elements of effective Coulomb coupling for Auger-like processes in NWs is very slow, and size dependence of the rates \( W_n \) is mainly governed by size-dependent overlap of phonon-broadened single- and bieexciton states.

Thus, despite strong spatial quantization of the transverse electron motion resulting in significant relaxation of translation-momentum conservation, temperature and size behavior of AR in NWs qualitatively differs from that in NCs. However, this effect is observed only in NWs with a strong interband coupling, and it is not described in the framework of particle-in-a-box model.

If carrier motions in the conduction and the valence bands are treated as independent of each other, envelope electronic wave functions in the cylindrical coordinate system \((r, \phi, z) \equiv (r, z) \) with the Z axis directed along the NW axis are easily found as \( \chi_{m_1,s_1} = J_{m_1}(pr)e^{im_1\phi}e^{iRz}\sigma_a \), where \( J \) is the Bessel function, and
and three-component envelope functions $i$ is a vector projection of the transverse motion on the structure is described by bispinors $\tilde{\psi}$, and the valence bands. The subband states are characterized by the total angular momentum projection $m_1$, two possible directions of the electron spin, and two possible directions of the wave vector $k$. Auger decay of the ground biexciton state is allowed, and the AR rate does not vanish at $T = 0$.

In the four-band envelope-function formalism, taking into account a strong coupling between the conduction and the valence bands, total electronic wave functions in lead-salt NCs and NWs are written as a product, $\psi = \sum_{i=1}^{4} F_i u_i$, of the four band-edge Bloch functions $u_i$ of the conduction ($i = 1, 2$) and the valence ($i = 3, 4$) bands, and four-component envelope functions $F_i$. The transverse electron motion in NWs is described by bispinors

$$\Psi_{\pm, m_j} = \frac{1}{\sqrt{4\pi \varepsilon_p}} \left( \sqrt{\varepsilon_p \pm \varepsilon_p f_{m_1}(r)} e^{\pm im_1 \phi} \sigma_1 \right),$$

$$\Phi_{\pm, m_j} = \frac{1}{\sqrt{4\pi \varepsilon_p}} \left( \sqrt{\varepsilon_p \pm \varepsilon_p f_{m_1}(r)} e^{\pm im_1 \phi} \sigma_1 \right),$$

where $m_1 = m_j - \frac{1}{2}$, $m'_1 = m_j + \frac{1}{2}$, $\varepsilon_p = \varepsilon_{p,k=0}$, and $\varepsilon_p = \sqrt{\varepsilon_p^2 + \eta^2 p^2}$ is the subband-edge energy, $\eta$ is a parameter of the interband coupling, and $f_{m_1}(r)$ are radial wave functions normalized to unity. The total electronic structure is described by bispinors

$$F_{\pm, m_j} = \frac{1}{\sqrt{2E}} \left( \sqrt{E \pm \varepsilon_p} \Psi_{+, m_j} \mp \sqrt{E \pm \varepsilon_p} \Phi_{-, m_j} \right) \frac{e^{ikz}}{\sqrt{L}},$$

and

$$G_{\pm, m_j} = \frac{1}{\sqrt{2E}} \left( \sqrt{E \mp \varepsilon_p} \Psi_{-, m_j} \pm \sqrt{E \pm \varepsilon_p} \Phi_{+, m_j} \right) \frac{e^{ikz}}{\sqrt{L}}$$

in the conduction ($+$) band with the eigenenergy $E = \sqrt{\varepsilon_p^2 + \eta^2(p^2 + k^2)}$, and in the valence ($-$) band with the eigenenergy $-E$, where $\varepsilon = \sqrt{\varepsilon_p^2 + \eta^2 p^2}$. Electronic subbands are characterized by the total angular momentum projection $m_j = m_1 + s_z = \pm \frac{1}{2}$, $\pm \frac{3}{2}$, $\pm \frac{5}{2}$, $\ldots$ on the $Z$ axis and the wave vector of longitudinal motion $k$.

Two distinct sets of spatially quantized wave vectors of the transverse motion $p_n$ and $q_n$ ($n = 0, 1, \ldots$) are found from boundary condition equations

$$\sqrt{\varepsilon_p + \varepsilon_p J_{m_1, -1} (pR)} \sqrt{\varepsilon_p + \varepsilon_p J_{m_1, +1} (qR)} = \sqrt{\varepsilon_p - \varepsilon_p J_{m_1, -1} (\lambda R)} \sqrt{\varepsilon_p - \varepsilon_p J_{m_1, +1} (\lambda R)}$$

for the bispinors $\Psi_+$ and $\Phi_+$, and

$$\sqrt{\varepsilon_p + \varepsilon_q J_{m_1, -1} (pR)} \sqrt{\varepsilon_p + \varepsilon_q J_{m_1, +1} (qR)} = \sqrt{\varepsilon_p - \varepsilon_q J_{m_1, -1} (\lambda R)} \sqrt{\varepsilon_p - \varepsilon_q J_{m_1, +1} (\lambda R)}$$

for the bispinors $\Psi_-$ and $\Phi_-$, where $\lambda = \sqrt{p^2 + \lambda_0^2}$, $\lambda_0 = \frac{2m}{\sqrt{2m} E_g + \eta^2}$, and $\varepsilon_p = \varepsilon_{p,k=0} + \frac{2m}{\sqrt{2m}} \eta^2$. Since the longitudinal motion mixes $\Psi_+$ and $\Phi_+$-bispinors in bispinors $F$, and $\Psi_-$ and $\Phi_-$-bispinors in bispinors $G$, Eqs. (a) and (b) determine spatially quantized wave vectors $p_n$ and $q_n$ for $F$- and $G$-subbands, respectively. Thus, the interband coupling completely lifts degeneration of transverse motion states, and subband states in a given $L$-valley are degenerate with respect to two possible directions of the wave vector $k$ only.

In terms of envelope functions, a matrix element of long-range Auger process in the conduction band for the ground biexciton state, shown in Fig. 1, is derived as

$$\Gamma_k = \int dr_1 dr_2 [F_{+, m_j}^\dagger (r_1) F_{+, m_j}^\dagger (r_2) - F_{+, m_j}^\dagger (r_1) F_{-, m_j}^\dagger (r_2)]$$

$$\times U(r_1, r_2) \frac{\Gamma_k}{2} e^{ikz} (r_1),$$

where the wave functions of the longitudinal motion $\frac{1}{\sqrt{L}} e^{ikz}$ are included into an effective Coulomb coupling

$$U(r_1, r_2) = \frac{1}{L^2} \int_0^L dz_1 dz_2 U(r_1, z_1; r_2, z_2)$$

$\times \exp\{i(k_1 - k'_1)z_1 + (k_2 - k'_2)z_2\}$,
where $U$ is the energy of both direct Coulomb coupling and interparticle coupling via medium polarization. Owing to conservation of the total angular momentum projection, an electron in the conduction band can be excited only to subbands with $m_j = \frac{1}{2}$.

Nearby subband edges, where the energy differences $E - \varepsilon$ in Eqs. (3) are small, the expressions for $F$- and $G$-bispinors are simplified:

$$F_+ \simeq \Psi_+ - \rho \Phi_-; \quad F_- \simeq \rho \Psi_+ + \Phi_-$$

$$G_+ \simeq \rho \Psi_+ + \Phi_+; \quad G_- \simeq \Psi_- - \rho \Phi_+,$$

where $\rho = \frac{\eta k}{2\pi a_0}$ is the ratio of the longitudinal interband coupling energy to the energy of the transverse motion. In PbSe material, the parameter of interband coupling $\eta \approx 0.31$ eV·nm, and, at small $k \sim 2\pi/L$ and $L \sim 10$ μm, the parameter $\rho$ is estimated to be of the order of $(2 - 5) \times 10^{-4}$ for PbSe NWs of the radius of $2 - 8$ nm.

Due to orthogonality of the spinors $\sigma_\uparrow, \sigma_\downarrow \cdot \sigma_\uparrow = 0$, $\Psi_-, \Phi_-$ and $\Phi_+$ are also orthogonal to each other, $\Psi_0, \Phi_0 = 0$. Therefore, a contribution of recombination process for an electron from $F_-$-subband and a hole from $F_-$-subband to the matrix element $\Gamma_g$ is proportional to $\rho$. Correspondingly, the contribution to the AR rate $W_g \sim \Gamma_g^2$ is of the order of $\rho^2 \sim 10^{-7}$, i.e., AR of the ground biexciton state is strongly suppressed.

In general, we derive the following selection rules for Auger-like processes valid for states with sufficiently small wave vectors of the longitudinal motion:

- electron-hole recombination is allowed (i.e., it does not bring the small factor $\rho$ into a matrix element of Auger-like process) only if an electron and a hole belong to different subbands: $F_+$ and $G_-$, or $G_+$ and $F_-;

- on the contrary, electronic intraband transitions are allowed only inside $F$- and $G$-manifolds, since a transition, in which an electron is transferred from $F(G)$- to $G(F)$-subband inside the conduction (valence) band, brings the small factor $\rho$ into a matrix element of the process.

The first excited biexciton states are constructed from the ground state, if one of electrons (holes) is transferred to the subband $G_{+, -\frac{1}{2}}$ ($G_{-, -\frac{1}{2}}$), and the expression for matrix element of Auger decay of the excited biexciton state illustrated in Fig. 2 is derived as

$$\Gamma_n = \int d\mathbf{r}_1 d\mathbf{r}_2 F_{+, -\frac{1}{2}}^\dagger (\mathbf{r}_1) F_{+, -\frac{1}{2}} (\mathbf{r}_2, p_n) \mathcal{U}(\mathbf{r}_1, \mathbf{r}_2) \times F_{+, -\frac{1}{2}} (\mathbf{r}_2) G_{+, -\frac{1}{2}} (\mathbf{r}_1), \quad (6)$$

where $\mathcal{U}$ does not depend on $R$ at small $\Delta k = |k_1 - k'_1| = |k_2 - k'_2| \ll R^{-1}$, and $n = 1, 2, \ldots$ numerates the spatially quantized wave vectors of the transverse motion $p_n$ of the excited electron, or, in other words, subbands $F_{+, -\frac{1}{2}}$ with different wave vectors $p_n$. Now recombination of $G$-electron and $F$-hole is allowed by the selection rules.

To conserve the total angular momentum projection an electron is excited to $F$-subbands with $m_j = -\frac{1}{2}$, since a transition to $G$-subbands brings the small factor $\rho$. Then, summarizing over all channels of Auger decay of the first excited biexciton states, we derive for the AR rate

$$W(T, R) = \frac{16\pi}{h} e^{-\Delta E_{xx}/T} \sum_n D(\delta E_n) \Gamma_n^2, \quad (7a)$$

where the function $D$ describes overlap of the phonon-broadened final single-exciton state of the energy $E_x$ and initial biexciton states of the energy $E_{xx}$ with the energy detuning $\delta E = E_{xx} - E_x$.

Since at present we do not have any dependable experimental data on shapes, characteristic widths and Stokes shifts of phonon-broadened electronic states in NWs, we use for the function $D$ a simplified integral form

$$D(\delta E) = \int g(E) g(E - \delta E) dE, \quad \text{assuming that the function } g(E) \text{ is the Lorentzian with the width } \gamma \text{ and the Stokes shift } \Lambda. \quad \text{Then, we finally find}$$

$$W(T, R) = \frac{16\pi}{h} e^{-\Delta E_{xx}/T} \sum_n \frac{\gamma}{(\delta E_n - 2\Lambda)^2 + \gamma^2} \Gamma_n^2, \quad (7b)$$

To characterize the AR efficiency for multie exciton states, we introduce a “linear” length-independent AR coefficient

$$C_L = W L^2, \quad \text{which is analogous to the AR coefficient in bulk materials.} \quad \text{Then, the AR time of multie exciton states is found as } \tau = (C_L n_L^2)^{-1}, \quad \text{where } n_L \text{ is the linear density of excitons.}$$

The results of numerical calculations of the linear coefficient $C_L$ with $\gamma = 20$ meV and $\Lambda = 50$ meV for PbSe NWs of the radius $2 - 8$ nm at $T = 300$ K are presented in Fig. 3. The total coefficient is the sum of coefficients $C_{L1}$ and $C_{L2}$, which correspond to AR processes with an electron excitation to subbands with the wave vectors $p_1$ and $p_2$, respectively.

Although numerical calculations are quite sensitive to unknown parameters of electron-phonon coupling, the
The AR coefficient $C_{\text{bulk}}$ in bulk PbSe was measured to be approximately constant between 300 and 70 K with a value of about $8 \times 10^{-28}\text{ cm}^6\text{/s}$, and then drops a value of about $1 \times 10^{-25}\text{ cm}^6\text{/s}$ at $T = 30\text{ K}$. The huge growth of the volume coefficient $C_V$ in NWs from $2.2 \times 10^{-30}$ ($R = 2\text{ nm};$ strongly suppressed AR) to $1.2 \times 10^{-25}\text{ cm}^6\text{/s}$ ($R = 8\text{ nm};$ greatly enhanced AR) is determined by increasing both the linear coefficient $C_L$ in a wide interval from $0.14 \times 10^{-3}$ ($R = 2\text{ nm}$) to $30 \times 10^{-3}\text{ cm}^2\text{/s}$ ($R = 8\text{ nm}$) and the NW volume.

It is easy to see that AR in NWs demonstrates a qualitatively different temperature behavior compared with that in bulk parent material: AR in NWs is temperature suppressed due to decreasing the population of excited biexciton states, which scales as $e^{-\Delta E_2/T}$, where $\Delta E_2$ is the excited biexciton states ranges in the interval from $117\text{ meV}$ ($R = 2\text{ nm}$) to $13\text{ meV}$ ($R = 8\text{ nm}$).

Overall, we have shown that owing to specific selection rules for Auger-like processes in lead-salt NWs with a strong coupling between the conduction and the valence bands, AR is strongly suppressed in “slim” NWs of the radius $R < 4\text{ nm}$ ($C_V < C_{\text{bulk}}$), but significantly enhanced ($C_V > C_{\text{bulk}}$) at $R > 4\text{ nm}$ in comparison with bulk PbSe material. Moreover, temperature dependence qualitatively differs from that in bulk parent material and NCs. Finally, size dependence is reversed to that in NCs: the AR rate is greatly reduced with decreasing the NW radius, while in NCs it grows as $R^{-3}$.

Ultrafast multieexciton decay via AR is a major impediment for prospective applications of semiconductor NCs in lasing. Therefore, suppression of AR of the ground biexciton state exhibiting strong radiative decay of electron-hole pairs with the dipole momentum mainly determined by the longitudinal Kane momentum of bulk material makes obviously quantum-confined lead-salt NWs a subject of special interest for numerous lasing applications in near- and mid-infrared spectral ranges.

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FIG. 3: Size dependence of the linear AR coefficients $C_{L1}$ (curve) and $C_{L2}$ (solid circles) in PbSe NWs of the radius of 2 – 8 nm.

The obtained results demonstrate basic trends in temperature and size behavior of the AR efficiency in NWs.

The matrix elements $\Gamma_1$ and $\Gamma_2$ depend on the NW radius very slowly, and size dependence of the AR efficiency is mainly governed by size-dependent overlap of phonon-broadened single- and biexciton states. Therefore, size dependence of the AR efficiency in NWs is reverse to that in NCs: It is greatly reduced with decreasing $R$, while in NCs, size dependence is mainly governed by size-dependent matrix elements of Coulomb coupling ($\propto R^{-1}$), and the AR rate scales as $R^{-3}$.

The coefficient $C_{L2}$ exhibits a strong resonance behavior due to vanishing $\delta E_2 - 2\Delta$ at the radius of about 6 nm, where the phonon-broadened single- and biexciton states are well overlap each other. Despite $\Gamma_2$ is much smaller $\Gamma_1$, $\Gamma_2 \approx 0.1\Gamma_1$, a contribution of the resonance channel to the total coefficient $C_{L}$ exceeds nearby resonance a contribution of the non-resonance channel, in which $\delta E_2 - 2\Delta \gg \gamma$ at all NW radii.

To compare AR efficiencies in NWs and bulk parent materials, it is illustrative to introduce a “volume” coefficient $C_V = C_L S^2$, where $S$ is the NW cross-section area.

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