Nonradiative trapping and localization in intermediate band solar cells

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Abstract—For intermediate band solar cells (IBSC) to achieve high efficiency, the gains in light absorption due to the intermediate band (IB) must exceed the nonradiative losses from mid-gap states. An important proposal holds that in IB's formed from bulk doping, when the energy states of the IB are delocalized (i.e., metallic), they do not significantly reduce the nonradiative lifetime. We show that this proposal is incorrect because the motion of the crystal lattice will always re-localize IB states. We compare this result to band-to-band nonradiative recombination, which is well known to be slow. For IBSC's to realize their potential, research must move away from delocalizing IB states.

Index Terms—charge carrier lifetime, photovoltaic cells, mathematical model.

I. INTRODUCTION

The intermediate band solar cell (IBSC) is a potentially transformative concept for high-efficiency photovoltaics [1]. An early version was proposed by Wolf [2], and in-depth theoretical analysis examined and rejected the Si:In system [3]. The IB concept – harnessing subgap light using states inside the semiconductor band gap – was given new life in 1997 by detailed balance calculations showing a maximum conversion efficiency of 63% in fully concentrated sunlight [1], considerably higher than the 41% concentrated Shockley-Queisser limit [4]. Since 1997, there has been much success in developing systems with intermediate bands for intermediate band solar cells (IBSC) [5]. However, intermediate levels deep in the band gap have long been known to be detrimental to carrier lifetime [6], [7]. For this reason, the IBSC has long been dismissed as impossible [8]. A pathbreaking and highly-influential proposal for IBSC's formed from deep-level dopants holds that delocalized (i.e., metallic) states in an intermediate band (IB) do not cause nonradiative recombination [9], [10]. According to this proposal, once such a metallic IB is formed, increasing the dopant concentration *increases* the carrier lifetime. This lifetime recovery proposal has launched a large effort to observe an insulator-to-metal transition in semiconductors doped with high concentrations of deep-level dopants [11]–[16], including experimental claims of lifetime recovery [17], [18].

We show that this proposal will not be effective, and an insulator-to-metal transition (IMT) in an intermediate band will not suppress multiphonon recombination processes. It is possible for carrier lifetimes to increase for other reasons (e.g., chemical changes, energy level shifts), but the delocalization of IB orbitals is necessarily too fragile to prevent nonradiative recombination. Progress in IBSC's requires overcoming the nonradiative recombination problem, but we show that the IMT is not a way forward for the field. The search for IMT's with deep-level dopants has led to great progress in materials science, and if these materials are sufficiently strongly absorbing of subgap light, they can still produce highly efficient solar cells [19].

The lifetime recovery proposal combines two true statements and arrives at an appealing but erroneous conclusion. A (true): at high impurity concentrations, impurity orbitals can overlap and become delocalized, which is called an insulator-to-metal transition. B (true): the nonradiative capture cross section of a defect generally decreases as the impurity orbital becomes larger. That is, as the impurity state delocalizes, the nonradiative lifetime should increase. C (false): an IMT in an intermediate band delocalizes the impurity orbitals and therefore suppresses nonradiative capture.

II. ARGUMENT AGAINST LIFETIME RECOVERY

In this paper, we carefully outline why the conclusion C does not follow from A and B, first described in Ref. [19]. We first go through these three steps in detail. We then compare to the case of band-to-band multiphonon recombination, which is well known to be slow due to the delocalized character of the conduction- and valence-band states. Finally, we describe the conditions under which lifetime recovery may still occur (not due to IMT) and the remaining loopholes in our derivation, none of which we believe would change our conclusions.

A. High dopant concentration causes delocalization

Metallic conduction at low temperature relies on delocalized energy eigenstates at the Fermi energy. IMT's have been observed in several shallow-doped semiconductor systems [20], [21]. These results have recently been extended to deep-dopant systems by groups developing IBSC's, including Si:S [12], Si:Se [13] and Si:Ti [15]. It is possible that in the deep-dopant transitions, the impurity band broadens to overlap the conduction band [13], which would make it unsuitable for IBSC.

B. For isolated defects, delocalization increases nonradiative lifetime

A defect-mediated recombination event consists of two trapping events: a conduction band (CB) electron is trapped into an empty defect level and a hole is trapped into a filled defect level. The original proposal for lifetime recovery [9] focused on the multiphonon mechanism for nonradiative trapping [22], [23], as opposed to other mechanisms such as cascade capture [24] and Auger recombination [25]. We will focus exclusively on multiphonon trapping and recombination, which we will refer to as simply nonradiative trapping and recombination. For convenience, we will consider only the
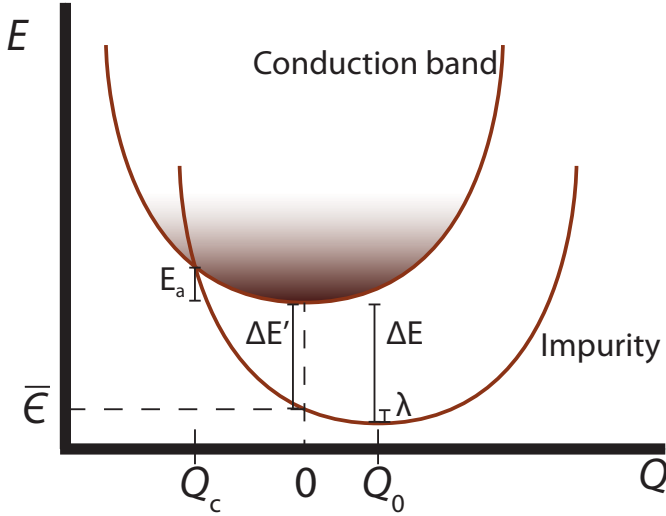
Q=0 Equilibrium with CB occupied   **Q=Q₀** Equilibrium with impurity occupied   **Q=Q_c** High-energy configuration
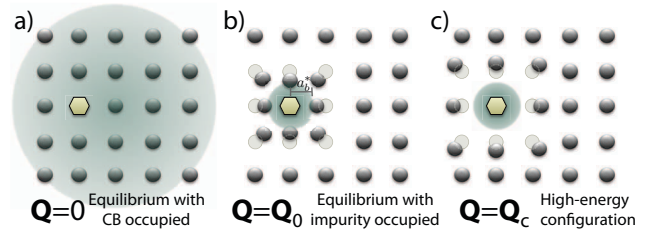
Fig. 2. Illustration of why localization causes recombination. Each panel is a cartoon of a semiconductor with an isolated impurity atom. a) An electron is in the conduction band, so its charge density is uniformly distributed through the sample. b) When the electron occupies the localized impurity state, the charge density is localized, and the nearby ions are attracted, moving to new equilibrium positions $\vec{Q}_0$. The effective Bohr radius a_b^* is shown. c) Trapping occurs in a lattice configuration $\vec{Q}_c$ where the ions destabilize the impurity state, raising its energy to be degenerate with the conduction band.

Fig. 1. Configuration coordinate diagram for trapping of a conduction band (CB) electron by an impurity level. The energy of the CB and impurity level are shwon as a function of a single harmonic vibrational mode with coordinate Q is depicted. Trapping occurs where the levels are degenerate. At high temperatures, trapping is an activated process with barrier E_a at lattice coordinate Q_c. As the impurity wave function becomes larger, Q_0 and λ approach 0, increasing both E_a and Q_c.

CB to IB trapping process, and all results are easily translated into the case of hole trapping from the valence band (VB).

We now present the standard description of the nonradiative trapping process [22], [23]. We model the system in the adiabatic approximation, valid when the electron motion is fast compared to the vibrational motion, allowing the electron problem to be solved separately for each lattice configuration [25]–[27]. The lattice vibrations can be described by normal modes with frequencies ω_i and coordinates Q_i. The physics is clearest when we neglect the lattice momenta and treat the Q_i as classical quantities. Trapping from a CB state into an impurity state occurs when the lattice is in a configuration where these two electronic states are degenerate, marked as Q_c in Fig. 1. We consider the high-temperature, activated limit, in which the trapping rate U is [25]

$$U \propto \exp\left(\frac{-E_a}{k_b T}\right), \qquad (1)$$

where T is the temperature, k_b is Boltzmann's constant, and E_a is the activation energy, as shown in Fig. 1. All of the main conclusions hold with low-temperature tunneling-based trapping, too [19]. In Fig. 1, there is only one vibrational mode shown and thus only one intersection; in a real system, there are many vibrational modes, and the lowest-energy degeneracy between the CB and impurity states determines E_a. From the geometry of the parabolae, it is easy to show that

$$E_a = \frac{\Delta E'^2}{4\lambda} = \frac{(\Delta E - \lambda)^2}{4\lambda}, \qquad (2)$$

where $\lambda = \Delta E - \Delta E'$ is the reorganization energy, indicated in Fig. 1, and this result is valid with many vibrational modes.

For shallow donors, the wave function is often approximated as a hydrogenic 1s orbital bound to the impurity, screened by the surrounding dielectric. For deeper donors, there is no

systematic accurate approximation for the wave functions. For a hydrogenic 1s orbital in a polar semiconductor,

$$\lambda \propto 1/a_b^*, \qquad (3)$$

where a_b^* is the effective Bohr radius, indicated in Fig. 2b [25], [27], [28], so larger orbitals give slower trapping. This result can easily be understood qualitatively by considering the effect of moving an electron from a delocalized conduction band state (Fig. 2a) to the localized impurity state (Fig. 2b). An electron charge that was evenly distributed over large numbers of lattice sites becomes localized. The nearby ions are attracted to it, shifting their equilibrium positions. This shift is precisely the move of equilibrium from $\vec{Q} = 0$ to $\vec{Q}_0$.

Let us examine Fig. 1 more carefully. When the electron-phonon coupling is linear in $\vec{Q}$, the vibrational frequencies are the same in the two electronic states, but the equilibrium position is different: 0 or $\vec{Q}_0$. As a_b^* increases, the electron density in the impurity state becomes less concentrated, so the shift of nearby ions when the impurity becomes occupied (illustrated in Fig. 2b) is reduced, reducing $\vec{Q}_0$. It is clear from Fig. 1 that this reduction increases E_a and thus decreases U. This effect is at the heart of the lifetime recovery proposal [9], and it is in this sense that *localization causes recombination*. But this effect is for isolated defects. We now show that delocalization that originates in superpositions of orbitals is less robust than this "delocalization" of a single orbital, as the electron-phonon interaction localizes the states.

C. *IMT delocalization* does not *increase nonradiative lifetime*

We now consider the case of trapping into an IB rather than an isolated impurity. We consider the best-case scenario for lifetime recovery: a perfectly periodic superlattice of impurities inside the host semiconductor. Disorder also poses problems for delocalization [16], [29], but disorder is not important for our argument here, though it is not harder to include [19]. We construct a model for the IB system and the electron-phonon coupling, taking care to discuss it in both localized and delocalized bases. We then give a variational argument showing that the delocalization of the IB can only increase the nonradiative lifetime [19].

We begin by considering the lattice in its equilibrium position when the IB is empty, $\vec{Q} = 0$. For convenience, we consider a single electron (initially at the bottom of the conduction band) with the IB states empty. We describe the states inside the IB using a localized basis $|\phi_{\vec{R}}\rangle$ and a delocalized basis $|\psi_{\vec{k}}\rangle$. We begin by taking the isolated impurity states localized at each impurity site $|\phi_{\vec{R}}\rangle$, orthogonalized appropriately, where $\vec{R}$ denotes the impurity locations.[1] As the impurity concentration increases, the electrons can hop between the sites and produce delocalized energy eigenstates $|\psi_{\vec{k}}\rangle$, where $\vec{k}$ denotes the crystal momentum in the superlattice of impurities. In the case of noninteracting electrons, the energy eigenstates are always delocalized, though when interactions are included this delocalization occurs only at a finite concentration [32]. These delocalized energy eigenstates form the second basis for this system; we could equally have arrived at them by invoking Bloch's theorem for a periodic system and noting that our energy eigenstates must be of the form $\psi_{\vec{k}} = e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})$, where $u_{\vec{k}}(\vec{r})$ is periodic with the superlattice periodicity.

We can write the Hamiltonian for the IB system as $H = H_e + E_{ph} + H_{e-ph}$, with

$$H_e = \bar{\epsilon} \sum_{\vec{R}} |\phi_{\vec{R}}\rangle\langle\phi_{\vec{R}}| + \sum_{\vec{R}\neq\vec{R}'} t_{\vec{R}\vec{R}'} |\phi_{\vec{R}}\rangle\langle\phi_{\vec{R}'}| \quad (4)$$

$$E_{ph} = \sum_i \omega_i^2 Q_i^2 / 2 \quad (5)$$

$$H_{e-ph} = \sum_{i\vec{R}\vec{R}'} Q_i A^i_{\vec{R}\vec{R}'} |\phi_{\vec{R}}\rangle\langle\phi_{\vec{R}'}|, \quad (6)$$

where $t_{\vec{R}\vec{R}'}$ is the matrix describing the hopping between localized states (i.e., $t_{\vec{R}\vec{R}'}$ describes the delocalizing forces, which become larger with impurity concentration). For each phonon mode i, A^i gives the effect of the lattice vibration on the electronic states, either changing on-site energies (diagonal terms $A^i_{\vec{R}\vec{R}}$) or hopping (off-diagonal terms $A^i_{\vec{R}\vec{R}'}$). There is, in addition, electron-phonon coupling between the IB and the CB, which is responsible for the actual transfer of electrons between these states. This coupling is important only when an IB state described by Eqs. 4-6 is nearly degenerate with the CB. We do not express these terms explicitly, but the nonradiative lifetime depends on their values [25]. If the largest (smallest) eigenvalues of t are $t_{1(2)}$, we define the IB bandwidth $J = (t_1 - t_2)/2$. We must have $J < \Delta E'$, or we do not have an IB.

We can also write

$$H_e = \sum_{\vec{k}} \epsilon(\vec{k}) |\psi_{\vec{k}}\rangle\langle\psi_{\vec{k}}| \quad (7)$$

$$H_{e-ph} = \sum_{i\vec{k}\vec{k}'} Q_i \tilde{A}^i_{\vec{k}\vec{k}'} |\psi_{\vec{k}}\rangle\langle\psi_{\vec{k}'}|, \quad (8)$$

with energies $\epsilon(\vec{k})$ and new matrices $\tilde{A}^i$, related to the A^i by a basis transformation. We further let $H_0 = H_e + H_{e-ph}$.

The bases $\phi_{\vec{R}}$ and $\psi_{\vec{k}}$ allow us to treat different effects easily. When $\vec{Q} = 0$, as in Fig. 2a, the $\psi_{\vec{k}}$ basis is the simplest, as the Hamiltonian is diagonal, and delocalized states

are a natural description. But as thermal fluctuations cause $\vec{Q}$ to vary, we must consider the A^i terms. In the delocalized $\psi_{\vec{k}}$ basis, the matrices $\tilde{A}^i$ are complicated and off-diagonal. The most important physical assumption that we make is that the main effect of the phonons is to change the on-site energies in the local basis, which is generally true in the adiabatic approximation [27], [28]. That is, the matrices A^i are approximately diagonal. This assumption means that as the lattice is distorted, the energy to occupy individual impurity sites changes, but the overlaps between the impurity wave functions, which affect the hopping t, do not change. As the lattice positions $\vec{Q}$ change and the eigenvalues of the matrix $\vec{Q}\cdot\vec{A}$ become larger than the bandwidth J, the phonons localize the energy eigenstates of the system, and the local $\phi_{\vec{R}}$ basis becomes a more useful basis to study the problem.

We now present the variational argument that delocalization does not increase the nonradiative lifetime [19]. We already know, from studying the isolated impurity problem in Section II-B, that there is a $\vec{Q}_c$ such that $\left|\phi_{\vec{R}_0}\right\rangle$ gains enough energy $\Delta E'$ to be degenerate with a conduction band state, with reference to Figs. 1 and 2c.[2] That is, when $t = 0$, the largest eigenvalue of $\vec{Q}_c \cdot \vec{A}$ is $\Delta E'$, and the eigenvector $|\rho_0\rangle$ is approximately one of the maximally localized states $|\phi_{\vec{R}_0}\rangle$ because we know by Eqs. 1-3 that trapping is fastest through the most localized states, as illustrated in Fig. 2.

If the IMT increases the nonradiative lifetime, it must be that E_a increases when the electrons are able to hop to other impurities (encapsulated in $t_{\vec{R}\vec{R}'}$), and having the lattice in configuration $\vec{Q}_c$ must no longer cause an IB state to become degenerate with a CB state. That is, the largest eigenvalue of $H_0(\vec{Q}_c)$ must be less than $(\bar{\epsilon} + \Delta E')$.

We know that $\left\langle\phi_{\vec{R}_0}\left|t\right|\phi_{\vec{R}_0}\right\rangle = 0$, and we expect in most systems that $\langle\rho_0|t|\rho_0\rangle = 0$, too. A finite $\langle\rho_0|t|\rho_0\rangle$ shifts the energy of the localized state and can increase or decrease the nonradiative lifetime, depending on its sign, but it is not caused by delocalization or an IMT – see Sec. IV-B1. A perturbative calculation of the effects of such terms is in Ref. [19]. Since we are only interested in studying the effects of delocalization, we therefore assume that $\langle\rho_0|t|\rho_0\rangle = 0$.

We then have $\langle\rho_0|H_0(\vec{Q}_c)|\rho_0\rangle = (\bar{\epsilon} + \Delta E')$. Therefore, by the variational principle, the largest eigenvalue of $H_0(\vec{Q}_c)$ must be greater than or equal to $(\bar{\epsilon} + \Delta E')$. The effect of delocalization across several impurities is only to possibly *increase* the capture cross section of each impurity, in addition to providing more recombination centers.

This result can be understood to mean that eigenstates initially delocalized across multiple impurity sites are localized by electron-phonon interactions. When $\vec{Q} = 0$, the eigenstates of the IB may be localized or delocalized. As thermal fluctuations bring the lattice into configuration $\vec{Q}_c$, the electron-phonon coupling H_{e-ph} is larger than the effects of t, since $\Delta E' > J$. Therefore, one of the localized states becomes an approximate eigenstate of the system and can become degenerate with the CB minimum, resulting in rapid

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[1]In non-dopant-based IB systems [30], [31], the localized basis can be constructed from Wannier functions, described in Section III.

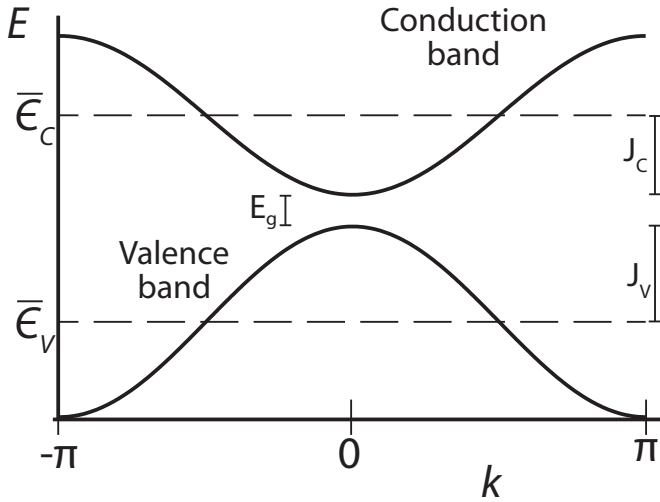[2] In a periodic system with N unit cells, there are N equivalent sites, and we consider one of them here.

Fig. 3. A simple 1D semiconductor band structure (energy vs. wavevector) illustrating the key energy scales: the band gap E_g, the bandwidths J_α, and the mean energy $\bar{\epsilon}_\alpha$, for $\alpha = C, V$. The nonradiative lifetime is determined by the energy gap $\bar{\epsilon}_C - \bar{\epsilon}_V$, which is generally much larger than E_g. Though this figure shows a direct-gap semiconductor, for our purposes it does not matter whether the semiconductor is direct or indirect.

trapping, just as in the case of independent impurities. Multi-site delocalization, as in an IMT, does not extend nonradiative lifetimes in the same way that increasing the size of a single-impurity state does.

III. COMPARISON TO BAND-BAND MULTIPHONON RECOMBINATION

We have shown that delocalization across many sites in an intermediate band does not increase the nonradiative lifetime compared to the case with independent sites. Yet it is well known that multiphonon recombination is slow (insignificant) for conduction- to valence-band recombination, which is often credited to the delocalization of the conduction and valence band wave functions. We now adapt the model described above to analyze the case of band-to-band recombination and illustrate why the nonradiative lifetime is so long. The essential reason is that the effective energy gap is much larger than $\Delta E'$.

We describe our CB and VB within an effective non-interacting model, as above. By Bloch's theorem, we can diagonalize the Hamiltonian in a basis of states with well-defined crystal-momentum $\vec{k}$. For convenience, we assume that each band has only a single state at each $\vec{k}$. Then we write

$$H_e = \sum_{\vec{k}} \epsilon_C(\vec{k}) \left| \psi_{C,\vec{k}} \right\rangle \left\langle \psi_{C,\vec{k}} \right| + \epsilon_V(\vec{k}) \left| \psi_{V,\vec{k}} \right\rangle \left\langle \psi_{V,\vec{k}} \right|, \quad (9)$$

where $\left| \psi_{C(V),\vec{k}} \right\rangle$ are states in the CB (VB). We define the bandwidth J_C (J_V) of the CB (VB) in Eq. 9 to be half the difference between the maximum and minimum energies in the band, as in Fig. 3. We construct localized states from these Bloch states using Wannier functions [33]. For an appropriate choice of phases on the Bloch states $\psi_{C(V),\vec{k}}$, these can be made maximally localized [34], and we call these localized

states $\left| \phi_{C(V),\vec{R}} \right\rangle$, where $\vec{R}$ are the centers of the unit cells of the crystal. That is, we write

$$\left| \phi_{C,\vec{R}} \right\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}} \left| \psi_{C,\vec{k}} \right\rangle, \quad (10)$$

where N is the number of unit cells in the system and the sum is over the first Brillouin zone; similar results apply for $\left| \phi_{V,\vec{R}} \right\rangle$. These localized states are not eigenstates of H_e, but we can express H_e as in a tight-binding model over these states.

$$H_e = \bar{\epsilon}_C \sum_{\vec{R}} \left| \phi_{C,\vec{R}} \right\rangle \left\langle \phi_{C,\vec{R}} \right| + \sum_{\vec{R} \neq \vec{R}'} t_{C,\vec{R}\vec{R}'} \left| \phi_{C,\vec{R}} \right\rangle \left\langle \phi_{C,\vec{R}'} \right|$$

$$\quad (11)$$

$$+ \bar{\epsilon}_V \sum_{\vec{R}} \left| \phi_{V,\vec{R}} \right\rangle \left\langle \phi_{V,\vec{R}} \right| + \sum_{\vec{R} \neq \vec{R}'} t_{V,\vec{R}\vec{R}'} \left| \phi_{V,\vec{R}} \right\rangle \left\langle \phi_{V,\vec{R}'} \right|,$$

where $\bar{\epsilon}_\alpha \equiv \sum_{\vec{k}} \epsilon_\alpha(\vec{k})/N$ is the mean energy in the $\alpha = C, V$ band, N is the number of unit cells in the system, and $t_{\alpha,\vec{R}\vec{R}'}$ is the hopping matrix element between sites $\vec{R}$ and $\vec{R}'$, which generally decays rapidly with $\left| \vec{R} - \vec{R}' \right|$. This basis allows us to think of the CB and VB states similarly to the impurity states of Sec. II-C.

We couple in the motion of the lattice, with E_{ph} as in Eq. 5 and H_{e-ph} modified to

$$H_{e-ph} = \sum_{\alpha i \vec{R}\vec{R}'} Q_i A^i_{\alpha,\vec{R}\vec{R}'} \left| \phi_{\alpha,\vec{R}} \right\rangle \left\langle \phi_{\alpha,\vec{R}'} \right|, \quad (12)$$

where the sum goes over all unit cells $\vec{R}$, vibrational modes i, and $\alpha = C, V$. We can equivalently write H_{e-ph} in the delocalized basis,

$$H_{e-ph} = \sum_{\alpha i \vec{k}\vec{k}'} Q_i \tilde{A}^i_{\alpha,\vec{k}\vec{k}'} \left| \psi_{\alpha,\vec{k}} \right\rangle \left\langle \alpha, \psi_{\vec{k}'} \right|. \quad (13)$$

As in the case with the IB, the key physical assumption we make is that A^i_α is an approximately diagonal matrix, which implies that $\tilde{A}^i_\alpha$ has large off-diagonal components. Physically, this assumption means that distortions of the lattice change the energies of localized states but do not cause hopping from localized states to far-away states. In the momentum-basis, distortions of the lattice mainly cause scattering between different $\vec{k}$ states.

We now analyze this problem similarly to Sec. II-C. The nonradiative process has an activation energy $E_a = E_{ph}(\vec{Q})$ with $\vec{Q}$ a lattice configuration where the lowest energy in the CB is degenerate with the highest energy in the VB. If the system has carriers that can recombine, these extremal states are always filled and empty, respectively. We find the $\vec{Q}_c$ satisfying the degeneracy condition and minimizing E_a. For the bands to become degenerate, the electron-phonon coupling must raise a VB state out of the band to approach the CB (or similarly a CB state must approach the VB). Here we consider the case that a VB state is raised to the CB. We assume that the CB states are not strongly modified by this lattice distortion, as this assumption produces the fastest nonradiative process. That is, we seek a degeneracy between a VB state and the

delocalized state $|\psi_{C,0}\rangle$ at the CB minimum, where we assume the CB minimum is at $\vec{k} = 0$, as illustrated in Fig. 3.

Let $E_V(\vec{Q})$ be the largest eigenvalue of $t_V + \vec{Q} \cdot \vec{A}_V$, and let the eigenvector be $|\rho_V\rangle$. To satisfy the degeneracy condition, we must find $\vec{Q}$ such $E_V(\vec{Q}) = \epsilon_C(0) - \bar{\epsilon}_V \equiv \Delta E_{\text{eff}}$. Using a standard Lagrange multiplier technique, as in [19], we find the minimal E_a to be

$$E_a = \frac{(\Delta E_{\text{eff}} - \langle \rho_V | t_V | \rho_V \rangle)^2}{4\lambda_{CV}}, \text{ where} \qquad (14)$$

$$\lambda_{CV} = \sum_i \frac{\langle \rho_V | A_V^i | \rho_V \rangle^2}{2\omega_i^2}. \qquad (15)$$

Since the state $|\rho_V\rangle$ has left the VB, it must be close to being an eigenstate of $\vec{Q}_c \cdot \vec{A}_V$, with t_V as a perturbation. In order to minimize E_a, $|\rho_V\rangle$ must be maximally localized[3] [25], and therefore $\langle \rho_V | t_V | \rho_V \rangle \approx 0$.

We see from Eqs. 2 and 14 that even if the reorganization energies λ, λ_{CV} are similar, the activation energy for band-to-band nonradiative recombination is much larger than for recombination through an impurity in the band gap; ΔE_{eff} is approximately equal to $E_g + J_V$ while the best case for a dopant is $\Delta E' = E_g$. Since semiconductor bandwidths are generally much larger than their band gaps, nonradiative trapping into a mid-gap level can be rapid while band-to-band nonradiative recombination is negligible. We generally expect band-to-band nonradiative recombination to have $\Delta E_{\text{eff}} \approx E_g + \min[J_V, J_C]$, as the band with smaller bandwidth is more easily localized by the electron-phonon coupling.

We note that for band-to-band nonradiative recombination, there are M unit cells per unit volume, which is much greater than the N impurities per unit volume in a doped system. In the band-to-band case, all M of these unit cells contribute to the recombination. But since U is suppressed exponentially by ΔE_{eff}^2, the band-to-band nonradiative process is negligible, despite the large number of independent lattice sites.

IV. LOOPHOLES

We now discuss situations that could cause the above arguments to break down. We do not believe any of these loopholes change our conclusions. We further discuss possibilities for lifetime recovery which are not based in the IMT.

A. Loopholes that could permit IMT-based lifetime recovery

1) Electron-phonon coupling is non-local: As emphasized above, the key physical assumption is that the electronic states most strongly coupled to the lattice vibrations are localized in space. This result is well known for polar semiconductors [25], [28], [35], with the intuition given in Fig. 2, and there are similar results with deformation-potential coupling in nanostructures [36], [37]. But if it were not true, our argument would fail. This assumption is also required, however, for the lifetime recovery proposal, which relies on delocalization to slow recombination, so it is not clear that this loophole would permit IMT-based lifetime recovery.

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[3]As in footnote 2, for a periodic system with M unit cells there are M such configurations $\vec{Q}_c$, and we choose one here.

2) The matrices $\vec{A}$ vary with t : In this paper, we consider increasing or decreasing the concentration of impurities by turning on or off the hopping matrix t in order to study the system with and without the IMT delocalization. We assume that $\vec{A}$ does not vary with t, as it does not vary in a tight-binding model. Consider, however, an IMT that produces delocalized states that have a different span than the $t = 0$ independent-impurity wave functions. That is, the orthogonalized independent-state wave functions are not superpositions of the delocalized eigenstates. Localized Wannier functions can still be constructed, and $\vec{A}$ should be approximately diagonal in the local basis. In that system, however, $\vec{A}$ of the metallic system is not necessarily related to $\vec{A}$ of the independent-impurity system, and we cannot make further analytical progress. If the delocalized system for some reason has $\vec{A}$ of smaller magnitude, the nonradiative lifetime will increase, giving lifetime recovery. In particular, if the maximally localized Wannier functions are larger than the independent-impurity wave functions, then we would expect $\vec{A}$ to be smaller in magnitude and thus the nonradiative lifetime to increase. We do not see why this loophole should occur, but we cannot rule it out with the methods used here.

3) Adiabatic approximation breaks down: Our discussion has been entirely in the adiabatic approximation. This approximation assumes that the electrons move much more rapidly than the ions, so the ions cannot follow the electron motion and instead feel only an effective averaged potential. We can then write the electron-phonon wave functions as products of electronic and lattice wave functions. The momentum of the lattice is important for describing the actual trapping process, where the electron transfers from one electronic state to another, but in this paper we have only been concerned with finding the lattice configurations where trapping can occur, so we have neglected the lattice momentum. This approximation allows us to write the Hamiltonian H_e and H_{el-ph} in the simple forms above.

The adiabatic approximation is valid when the relevant electronic energies are much larger than the phonon energies [38]. The trapping process itself requires nonadiabatic effects, but only in the near vicinity of degeneracy [22], [23]. As the lattice approaches configuration $\vec{Q}_c$, where the relevant energy levels are degenerate, the corrections to adiabatic coupling cause the transfer from one electronic state to the other. This breakdown of the adiabatic approximation is not a loophole but rather a fundamental part of the trapping process.

If the adiabatic approximation is more generally invalid outside the vicinity of degeneracy, then all of these results are suspect. It is breaks down via polaron formation, then delocalized states are not formed. It is not clear whether a more general breakdown could be associated with lifetime recovery.

4) The linear-coupling approximation is invalid near $\vec{Q}_c$: The linear-coupling approximation of Eq. 6 is not itself well justified but is widely used, because it results in relatively tractable problems. If the electron-phonon coupling is non-linear in $\vec{Q}$, we expect all of the above results to hold qualitatively, but we have not proved that assertion.

5) Interaction effects: While this paper has used models of non-interacting electrons, we cannot rule out that correlated

many-body states could have other effects, as in Sec. IV-A2. We expect that the general result – that multi-site delocalized states are localized by electron-phonon interactions when the electron-phonon energy is larger than the bandwidth – remains true in interacting systems.

B. Other possibilities for lifetime recovery, not related to IMT

We now present reasons unrelated to IMT that lifetime recovery could still occur, though all of these effects could make lifetimes increase or decrease.

1) Shifts of $\bar{\epsilon}$: As more states are added to the IB, the intermediate energy levels could shift into or out of the gap, changing $\Delta E'$ and thus E_a as indicated in Eq. 2. In the notation of Sec. II-C, this consists of diagonal terms of the matrix $t_{\bar{R}\bar{R}}$. This effect could be very significant, though it is not related to IMT.

2) Shifts of the CB/VB: The formation of the IB could shift the CB and VB energies, due to chemical bonding or screening effects, which could also affect the nonradiative lifetime.

3) Chemical changes with concentration: As dopants are added to an IB material, they may undergo chemical changes, forming precipitates or occupying different structural states in the semiconductor. These can change the nonradiative lifetime.

V. SUMMARY

Progress in producing highly-efficient IBSC's requires extending nonradiative lifetimes. We show that even for an IB that is metallic when the lattice is in its equilibrium configuration, the delocalized states are fragile; as the lattice vibrates, localized states emerge from the IB to cause nonradiative trapping. The delocalization of the band can only *increase* the trapping rates. Progress in IBSC's will not occur by searching for delocalized intermediate bands.

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