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Nonradiative lifetimes in intermediate band photovoltaics—Absence of lifetime recovery

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Intermediate band photovoltaics hold the promise of being highly efficient and cost effective photovoltaic cells. Intermediate states in the band gap, however, are known to facilitate nonradiative recombination. Much effort has been dedicated to producing metallic intermediate bands in hopes of producing *lifetime recovery*—an increase in carrier lifetime as doping levels increase. We show that lifetime recovery induced by the insulator-to-metal transition will not occur, because the metallic extended states will be localized by phonons during the recombination process. Only trivial forms of lifetime recovery, e.g., from an overall shift in intermediate levels, are possible. Future work in intermediate band photovoltaics must focus on optimizing subgap optical absorption and minimizing recombination, but not via lifetime recovery. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4732085]

The development of novel highly efficient photovoltaic (PV) devices has the potential to significantly address the global energy and carbon problems. The vast majority of commercial solar cells are made from single-junction semiconductors, an architecture which Shockley and Queisser showed has an absolute efficiency limit of 41% (with concentrated sunlight).[1] Among the proposals to break this limit is the intermediate band (IB) photovoltaic, which has the considerably higher efficiency limit of 63%.[2–4]

The most important issue in choosing a material for a standard single-junction semiconductor PV is a tradeoff between current and voltage; these compete because it can absorb only photons with energy greater than the band gap E_g, and the supplied voltage can be no larger than E_g/e, where $-e$ is the electron charge. An IBPV device, illustrated in Fig. 1, has an extra set of levels inside the semiconductor band gap; two subgap photons can be absorbed by the IB layer, producing a single electron-hole pair. Electrical contact is made only to the standard n- and p-type layers, so the IB layer produces extra current while allowing the full band gap to set the limit on the voltage, giving the considerably elevated efficiency bound of 63%.[2] The IBPV effect has been demonstrated[5–7] and proposed[8,9] in a number of systems, though it has not yet produced high efficiency cells.

One method for making a material with an IB is to dope a semiconductor with large concentrations of impurities that form donor (or acceptor) levels deep inside the band gap. There is an obvious problem with this recipe: levels deep in the band gap are well known to cause nonradiative recombination,[10,11] which threatens to remove any advantage from the increased absorption. It was proposed that a sufficiently high concentration of dopants could cause an insulator to metal transition (IMT) in the IB, which would suppress the nonradiative recombination rate and cause *lifetime recovery* in which adding additional dopants decreases the nonradiative recombination rate.[12] A great deal of work has gone into looking for such an IMT in doped semiconductors,[13–19,52] including an experimental report of lifetime recovery.[20]

A single defect-mediated recombination event consists of two trapping events: a conduction band (CB) electron is trapped by an unoccupied defect state and a valence band (VB) hole is trapped by an occupied defect state. The statistical mechanics of the occupancy of the trap levels—showing that midgap states are best at fostering nonradiative recombination—was worked out by Shockley and Read[10] and Hall[11] and is called SRH recombination. The theoretical claim of lifetime recovery arose from a study of multiphonon recombination, the theory of which is well developed for isolated impurities.[21–24] When applied to polar semiconductors, that theory implies that the trapping rates decrease as the size of the defect wavefunction increases.[24,25] Since metallic systems have delocalized states, this result was taken to imply that midgap metallic states would not induce recombination.[12]

Here, we extend the multiphonon recombination theory to the case of many impurities. We show that many-impurity

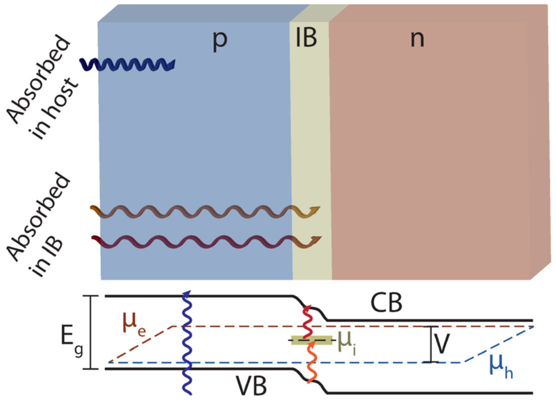

FIG. 1. An IB device has an IB layer between standard p- and n-type semiconductor layers. The IB layer absorbs subgap photons, which pass through the p-type (or n-type) host layer, increasing current generation. At bottom, band levels under illumination are shown, indicating the voltage V and the three separate quasi-Fermi levels μ_e, μ_h, and μ_i for the CB electrons, VB holes, and IB states, respectively. If trapping rates are low, voltage production is still determined by the n- and p-type band gaps.

delocalized states actually *increase* trapping rates compared to an equivalent localized system. We show that as long as the shift of IB energies due to interactions in the IB is less than the dopant ionization energy $\Delta E'$, the trapping rates cannot be significantly reduced from the independent-dopant limit, regardless of whether the IB eigenstates are extended or localized. Trivial forms of lifetime recovery are still possible. For example, if the dopant chemical state changes with doping (e.g., if precipitates form), the recombination rate may drop with increased doping. Another trivial effect occurs if the interaction between defects moves the IB away from mid-gap, but this is not a useful route to IBPV, as the optical absorption frequencies will change accordingly.

Despite this negative prediction about true lifetime recovery, IBPV still has potential to produce highly efficient solar cells if materials can be found which have sufficiently strong absorptivity for subgap photons, as we discuss in the last section of this paper. Efforts should be directed toward finding semiconductor:dopant systems which have intrinsically long trapping times and in which the subgap absorptivities are high, not toward finding insulator-to-metal transitions in doped semiconductors.

We begin with an outline of the standard theory of multiphonon recombination for isolated dopants. We show how to extend this model to dopant concentrations where the intermediate band has a finite bandwidth, giving an intuition for why an IMT will not suppress trapping. We give a variational argument that such IB's will always increase the trapping rate, except for trivial effects. We then give a perturbative treatment, allowing bounds on the trapping rates from readily measured material properties. We conclude with a discussion of material requirements for functioning IBPV. Full details of the model and proofs are in the Appendix, as are discussions of interaction effects in a partially filled IB, applications to highly mismatched alloys (HMA), and the low-temperature (tunneling) limit of multiphonon trapping.

I. TRAPPING RATE

We consider a CB electron (equivalently a valence band hole, but we will consider an electron for specificity) captured by an unoccupied defect state. The argument for lifetime recovery focuses on multiphonon recombination, and we will consider that mechanism here. For neutral defects and deep defect levels, the multiphonon trapping mechanism is believed to be most important; in other cases cascade capture[26] or other mechanisms[27] can be important.

The basics of multiphonon recombination for isolated defects are illustrated in Fig. 2. We consider a simplified system with a single (initially occupied) conduction band state, a single impurity state, and one electron. We work in the Born-Oppenheimer approximation, and the motion of the lattice is treated classically (tunneling is considered in the Appendix). Vibrations of the lattice can be decomposed into normal modes, phonons, each with a frequency ω_i and a coordinate Q_i. As the lattice moves, the energy of the system changes due to two effects: the quadratic energy cost of distorting these phonon modes, $E_{ph} = \sum_i \omega_i^2 Q_i^2/2$, and a linear electron-phonon coupling, which depends on the electronic state of the system. We take $\vec{Q} = 0$ to be the equilibrium configuration with the electron in the CB state.

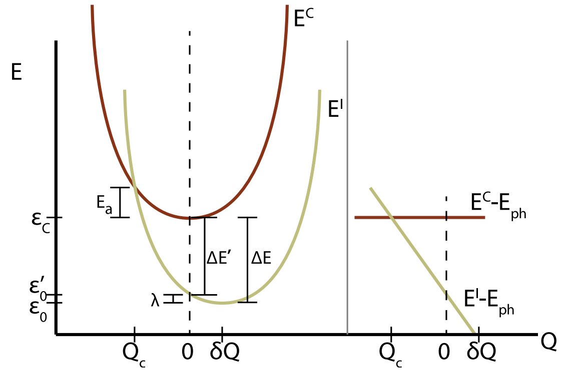

FIG. 2. For a system with one electron and one impurity, the configuration coordinate diagram at left shows energy levels as a function of lattice distortion Q with the electron in the CB (upper) and with the electron in the impurity state (lower). The equilibrium lattice coordinate is shifted to δQ when the localized impurity state is occupied, giving the relaxation energy λ and causing the parabolas to cross. The activation energy E_a shows the energy required to bring the CB electron to the degeneracy point, from which trapping occurs most rapidly. At right, the same state energies are displayed without the phonon energy E_{ph}, clearly showing the linear electron-phonon coupling. The two states are degenerate when the electron phonon coupling equals $\Delta E'$.

Figure 2 shows the energy of the two electronic states as a function of lattice distortion in one of the system's normal modes. The CB edge and unoccupied defect state have energies ε_C and ε_0', respectively. If the localized impurity state is occupied, the nearby ions are drawn toward the impurity, shifting their equilibrium position, and reducing the energy of the occupied state to ε_0, illustrated in the bottom curve. The relaxation energy $\lambda = \varepsilon_0' - \varepsilon_0$ is shown in the figure. With electron-phonon coupling linear in the phonon coordinates Q_i, the curvature of the parabola is the same in both electronic states.

When the lattice is in configuration Q_c, the conduction and impurity states are degenerate, which allows rapid transfer between them, i.e., trapping. The activation energy $E_a = \omega^2 Q_c^2/2$ shows how much energy is required to bring the CB state up to that degeneracy point. Simple algebra gives

$$E_a = \frac{(\Delta E')^2}{4\lambda} = \frac{(\Delta E - \lambda)^2}{4\lambda}. \tag{1}$$

In the high temperature limit, the resulting trapping rate is an activated process, with rate

$$\gamma = \frac{|V(\vec{Q}_c)|^2}{\hbar}\left(\frac{\pi}{k_B T \lambda}\right)^{1/2} \exp\left(-\frac{E_a}{k_B T}\right), \tag{2}$$

where T is the temperature, k_B is Boltzmann's constant, $\hbar$ is Planck's constant, and the $V(\vec{Q}_c)$ gives the phonon-induced coupling between the CB and impurity states, discussed further in the Appendix.[24] This is the same result as in Marcus theory, in whose terminology the IB trapping problem is generally in the inverted regime.[28]

In the case of polar electron-phonon coupling, $\lambda \propto 1/a_B^*$, where a_B^* is the effective Bohr radius of the hydrogenlike impurity wavefunction.[25,29,30] As the defect state spreads out, λ

decreases, increasing E_a and suppressing γ. Similar effects are found for deformation-potential coupling in confined systems.[31,32] Since the argument for lifetime recovery relies on this relationship, we will assume that it applies.

Equation (1) is also true when all the phonon modes are considered. In this case,

$$E_a = \frac{1}{2}\sum_i \omega_i^2 Q_{c,i}^2, \qquad (3)$$

where $\vec{Q}_c$ is the lattice coordinate such that $E^C = E^I$ and E_a is minimized.

A. Intermediate band

For large impurity concentration N_t, the impurity states can undergo an IMT, with an associated delocalization of the electron density in at least some of the IB eigenstates. Since λ decreases with impurity wavefunction size, Luque *et al.* suggested that the IMT would suppress the trapping rates and thus the overall recombination rate.[12] We show that the extrapolation from the isolated-impurity problem to the many-impurity problem is more complicated. Even when the IB has extended eigenstates, lattice distortions localize electronic states sufficiently to cause multiphonon recombination. The delocalized states in fact can only *increase* the trapping rate.

The key idea for generalizing the isolated-impurity result is that trapping occurs through the lattice configuration $\vec{Q}$ such that

1. A CB and an IB state are degenerate, and
2. The activation energy $E_a = \sum_i \frac{1}{2}\omega_i^2 Q_i^2$ is minimized.

Our goal is then to find the smallest E_a such that an IB state crosses the CB edge, which gives γ.

The band edges of the IB should be relatively easy to determine optically, so we consider the energies ε_1 and ε_2 of the highest and lowest energy states in the IB to be known. As shown in Fig. 2, ε_0' is the energy of the empty defect state in the dilute limit. Let $\Delta = \max\{|\varepsilon_1 - \varepsilon_0'|, |\varepsilon_2 - \varepsilon_0'|\}$ be the largest energy shift of an IB energy due to the many-impurity physics. Then $\Delta/\Delta E'$ will be our perturbation parameter, assumed to be small.

Our intuitive argument is that the lattice distortions required for multiphonon recombination necessarily localize the IB states. We know from the isolated-dopant case that a lattice distortion $\vec{Q}_c$ produces sufficient electron-phonon coupling to raise the energy of an unoccupied defect state by $\Delta E'$. Since the IB has a bandwidth no bigger than Δ, in IBPV systems (where $\Delta E' \gg \Delta$) the electron-phonon coupling in lattice position $\vec{Q}_c$ is much larger than whatever interactions in the IB cause delocalization. Regardless of whether the IB states are delocalized when $\vec{Q} = 0$, when the lattice is at $\vec{Q}_c$, the isolated-impurity wavefunction will be an approximate eigenstate of the system and thus allow multiphonon recombination, as illustrated in Figure 3. That is, the thermal (or tunneling) motion of the lattice responsible for the standard isolated-defect multiphonon trapping process also localizes many-dopant IB states.

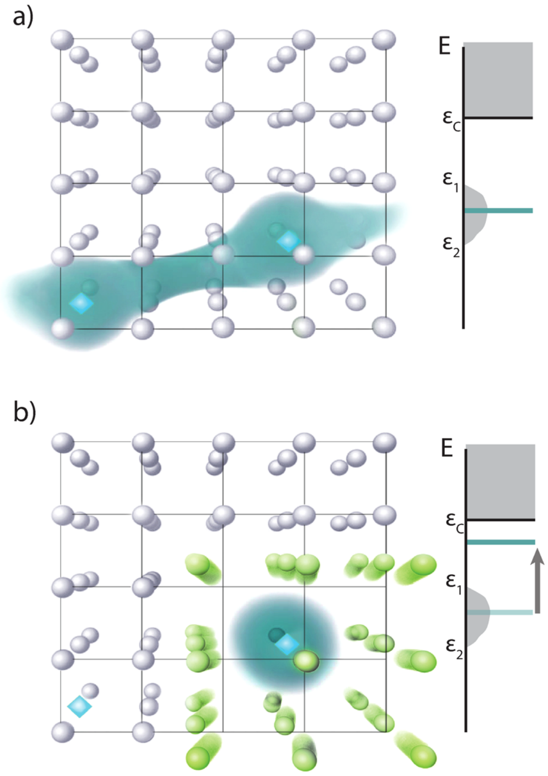

FIG. 3. Cartoon of a crystal of gray spherical atoms with blue diamond impurities showing the physical origin of phonon-induced localization. (a) With the intermediate band unoccupied and the atoms in their ground state positions, an eigenstate in the IB (light green) may be extended across the impurity sites. Its energy is indicated by the green line in the density of states (DOS), at right, which shows the conduction band and the intermediate band. (b) When a thermal fluctuation moves the atoms surrounding an impurity away from their equilibrium positions, an eigenstate becomes localized at that impurity; its energy is shown by the green line in the DOS. This occurs because for sufficiently large deviations of the host atoms, the electron-phonon coupling energy is larger than the IB bandwidth, so the eigenstates of the electron-phonon coupling become approximate eigenstates of the IB. When the energy of this localized state equals that of the CB, rapid trapping occurs.

Only when Δ is of similar order to $\Delta E'$ is it possible for the IB to have extended states that are still extended when $\vec{Q} = \vec{Q}_c$. In order to realize the Luque *et al.* proposal for lifetime recovery,[12] the IB must approach this large-bandwidth limit, having extended states and sufficient bandwidth to resist their localization. However, when Δ approaches $\Delta E'$, the IB crosses with the CB, and the material is no longer useful for IBPV. Note that both the CB and VB have bandwidths much greater than E_g, so their states are not easily localized, and there is no fast band-to-band multiphonon recombination process, as is well known.

Trivial forms of lifetime recovery may occur. Both SRH statistics and the dependence of γ (Eq. (2)) on ionization energy $\Delta E'$ produce the result that recombination is fastest through states at the center of the band gap, since recombination is limited by the slowest trapping process. We are assuming that both CB and VB trapping processes are dominated by direct multi-phonon processes and not cascade trapping. Thus, a perturbation that moves IB energy levels uniformly away from the center of the band will decrease the recombination rate. This trivial form of lifetime recovery is possible, but a suppression of recombination due to delocalization arising from an insulator-to-metal transition is not.

B. Variational argument

We now present a variational argument that delocalization in an IB always increases the trapping rate. We consider a system with N identical defects producing midgap states. As detailed in the Appendix, we take the basis of independent states localized on each impurity, $\{\psi_\alpha\}$ with $\alpha = 0 \ldots N-1$. These states are the eigenstates in the absence of impurity-impurity interactions. Interactions are given by the Hamiltonian term h, which couples the $\{\psi_\alpha\}$ to each other. The Hamiltonian is written out formally in Eq. (A1), in the Appendix. Let $\tilde{H}(\vec{Q})$ be the Hamiltonian containing only h and the electron-phonon coupling; let $E_0(\vec{Q})$ be the highest eigenvalue of $\tilde{H}(\vec{Q})$. Trapping occurs at the $\vec{Q}$ such that $E_0(\vec{Q}) = \Delta E'$ and E_a is minimized.

We consider an IB in which the bandwidth is less than $\Delta E'$, so the IB does not overlap with the CB when $\vec{Q} = 0$. With $h = 0$, let $\vec{Q}_0$ be the phonon coordinate such that $E_0^{h=0}(\vec{Q}_0) = \Delta E'$ and the activation energy, $E_a^{h=0}$, is minimal.[33] Let $|\psi_0\rangle$ be the associated eigenstate; $|\psi_0\rangle$ is localized since $h = 0$ and trapping is fastest through localized states. We now allow h to be nonzero and assume that $\langle\psi_0|h|\psi_0\rangle = 0$, to eliminate the trivial change of trapping rates due to shifts in the localized states' energies. By the variational principle, $E_0(\vec{Q}_0) \geq \Delta E'$, since $\langle\psi_0|\tilde{H}|\psi_0\rangle = \Delta E'$. We assume that $E_0(\vec{Q})$ is a smooth function of $\vec{Q}$. Then since by assumption $E_0(\vec{Q} = 0) < \Delta E'$, there is a $\kappa \leq 1$ such that $E_0(\kappa\vec{Q}_0) = \Delta E'$. The activation energy for this state is $E_a = \kappa^2 E_a^{h=0}$. Thus, the trapping rate is greater than or equal to the trapping rate without h at all.

C. Perturbative argument

The variational result is non-constructive. To understand its physical origin, we perform a perturbative calculation in h to find E_a as delocalizing effects are included. This also allows us to make a prediction for trapping rate changes, including the trivial effect. To second order in Δ, the activation energy is

$$E_a = E_a^0\left[\left(1 - \frac{h_{00}}{\Delta E'}\right)^2 - \frac{2}{\Delta E'}\sum_{\alpha>0}\frac{|h_{\alpha 0}|^2}{E_0 - E_\alpha}\right]. \tag{4}$$

Details of the derivation are in the Appendix. We use the notation $h_{ab} \equiv \langle\psi_a|h|\psi_b\rangle$, and E_α are the electron-phonon energies of the states ψ_α when $\vec{Q} = \vec{Q}_0$ and $h = 0$. As in the variational argument, E_0 is the highest eigenvalue of the electron-phonon coupling, chosen so $E_0 = \Delta E'$.

The second order correction to E_a (the second term in Eq. (4)) is always negative, since $E_0 > E_\alpha$ for all $\alpha > 0$, thus increasing γ. These are the terms resulting from the off-diagonal components of h, which can cause delocalization and which the variational argument showed always increase the trapping rate. The first order correction is the trivial change, which takes the activation energy for the localized states, Eq. (1), and shifts the energy gap $\Delta E'$ by h_{00}.

We can use this result to find an upper bound on E_a (and associated lower bound on γ), which is valid through second order. We consider h_{00} to be unknown, though it could be easily determined within a model for the IB. For example, a standard tight-binding model for the IB would have $h_{00} = 0$. Since we consider the IB band edges ε_1 and ε_2 to be experimentally determinable, we know $h_{00} \geq \varepsilon_2 - \varepsilon_0'$. Then we can bound, to second order,

$$E_a \leq \frac{(\varepsilon_C - \varepsilon_2)^2}{4\lambda_0}, \tag{5}$$

where ε_C is the CB edge, shown in Fig. 2.

If there are N defects (equivalently, N distinct IB states), then each one has an associated $\vec{Q}_c$, whose influence on trapping we can estimate in this same way. Then Eqs. (2) and (5) give a lower bound on the overall trapping rate for CB electrons that scales with N, just as for independent defects.

II. PROSPECTS FOR IBPV

Though nontrivial lifetime recovery in an IB system appears impossible, there is still good reason to think that IB devices can improve PV efficiencies. Consider an IBPV device as illustrated in Fig. 1. The high-energy photons will be absorbed by the p-type region before reaching the IB layer. Let α be the mean absorptivity of the IB region over the subgap portion of the spectrum. The IB layer width w must be sufficiently wide to absorb a large fraction of subgap photons, so it is desirable to choose $w = c/\alpha$ for $c \approx 2-3$. For the IBPV device to outperform the single-junction device with no IB, the IB region must add more current by absorption of subgap photons than it subtracts by enhanced nonradiative recombination, in addition to not significantly changing the voltage.

Let t be the transit time for a CB electron to move from the p-type to n-type side of the device and let τ be the nonradiative lifetime of CB electrons in the IB region. For the IBPV device to have higher efficiency than the single-junction device and approach the radiative limiting efficiency, it must have $\nu \equiv \tau/t \gg 1$. If we assume that the built-in voltage V_{bi} is dropped mostly across the thin IB region, then

$$t = \frac{w^2}{\mu V_{bi}}, \tag{6}$$

where μ is the electron mobility in the IB region. Alternatively, we could consider the time to diffuse across the IB region, also with $t \propto w^2$. Thus, for an IB region just thick enough to absorb the subgap light,[34]

$$\nu = \frac{1}{c^2}V_{bi}\mu\alpha^2\tau. \tag{7}$$

We roughly expect $\tau \propto 1/N_t$ and $\alpha \propto N_t$ in the IB region. The mobility also declines as $N_t^{-\beta}$, but generally with a small exponent β.[35,36] Thus, we have reason to believe that high dopant concentrations and strong subgap absorptivities[37–40] can produce useful IBPV devices. Full analysis balancing recombination and current generation as in Refs. 41–44 is required to evaluate particular systems.

Future research efforts should focus on producing highly absorptive, thin layers of IB materials made of dopants which have small contributions to nonradiative recombination, not on lifetime recovery. Non-dopant-based IBPV proposals, including highly mismatched alloys[5] and crystalline systems[45] may have inherently small trapping rates, so are also promising.

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APPENDIX: DETAILS OF MODEL, CALCULATIONS, AND APPLICABILITY

1. Model

As mentioned in the main text, we work in the Born-Oppenheimer approximation, in which the lattice is considered static for the electronic system, so we neglect the phonon momentum; each phonon coordinate Q_i has an associated angular frequency ω_i, and there are N impurities. We consider a situation in which there is initially one electron in the CB in a state $|\phi_c\rangle$, and all IB states are empty. This situation permits a single-electron picture with N localized orthogonalized impurity wavefunctions $|\psi_\alpha\rangle$ for $\alpha = 1 \ldots N$. We discuss effects of partial filling of the IB at the end of this Appendix. In this approximation, we ignore scattering by CB states into each other, which is valid in the usual case that the CB bandwidth is large compared to the electron-phonon coupling. Assuming linear coupling between the electron and phonon degrees of freedom, the Hamiltonian can be written as $H = H_{el} + E_{ph} + H_{el-ph}$ with

$$\begin{aligned} H_{el} &= \varepsilon_C|\phi_c\rangle\langle\phi_c| + \varepsilon_0'\sum_\alpha|\psi_\alpha\rangle\langle\psi_\alpha| + \sum_{\alpha\beta}h_{\alpha\beta}|\psi_\alpha\rangle\langle\psi_\beta| \\ E_{ph} &= \sum_i\frac{1}{2}\omega_i^2Q_i^2 \\ H_{el-ph} &= \sum_i Q_i\Big[\sum_{\alpha\beta}A^i_{\alpha\beta}|\psi_\alpha\rangle\langle\psi_\beta| \\ &\quad + \sum_\alpha B^i_\alpha(|\psi_\alpha\rangle\langle\phi_c| + |\phi_c\rangle\langle\psi_\alpha|)\Big], \end{aligned} \tag{A1}$$

where ε_C is the energy of the conduction band edge, ε_0' is the energy of the empty isolated-impurity state, the IB Hamiltonian h is zero in the dilute-impurity limit, A^i is responsible for the shift in the equilibrium phonon coordinate when an impurity state is occupied, and B^i causes the transition between the conduction and impurity states. In what follows, we will neglect B^i in describing state energies, as it is important only when IB and CB states are nearly degenerate. The phonon mass has been incorporated into the phonon coordinates (lattice displacements) Q_i. The phonon modes include all standard crystalline extended modes in addition to any local vibrational modes around the impurities.

2. Trapping rates

a. Isolated defects

We first re-express the standard results by considering the case of only one impurity, $N = 1$, so $h = 0$. If the electron is in the CB level, then the energy of the system is $E^C(\vec{Q}) = \varepsilon_C + \sum_i \omega_i^2 Q_i^2/2$. If the electron is in the impurity level, then the energy is

$$E^I(\vec{Q}) = \varepsilon_0' + \sum_i \frac{1}{2}\omega_i^2(Q_i + A^i/\omega_i^2)^2 - A^{i2}/2\omega_i^2.$$

We see that the equilibrium phonon position is $\delta Q_i = -A^i/\omega_i^2$. We define the relaxation energy $\lambda \equiv \sum A^{i2}/2\omega_i^2$. When the impurity state is filled, its relaxed energy is $\varepsilon_0 = \varepsilon_0' - \lambda$, as shown in Fig. 2. We also define $\Delta E' = \varepsilon_C - \varepsilon_0'$ and $\Delta E = \varepsilon_C - \varepsilon_0$, where primes indicate empty IB levels. It is customary to define the dimensionless Huang-Rhys factor for each phonon mode as

$$S_i \equiv \omega_i \delta Q_i^2/2\hbar = A^{i2}/2\hbar\omega_i^3, \tag{A2}$$

where $\hbar$ is Planck's constant. The total Huang-Rhys factor is $S = \sum_i S_i$. Then $\lambda = \hbar\sum_i S_i\omega_i$.

The energies E^C and E^I are equal when the phonon coordinate is such that $\vec{Q} \cdot \vec{A} = \Delta E'$. The activation energy to reach this configuration is $E_a = \sum_i \omega_i^2 Q_i^2/2$. The phonon coordinate $\vec{Q}$ satisfying $E^C(\vec{Q}) = E^I(\vec{Q})$ and minimizing E_a is denoted $\vec{Q}_c$. A simple application of Lagrange multipliers shows that

$$Q_{c,i} = \frac{A^i}{\omega_i^2}\frac{\Delta E'}{2\lambda}, \tag{A3}$$

which gives

$$E_a = \frac{1}{2}\sum_i \omega_i^2 Q_{c,i}^2 = \frac{(\Delta E')^2}{4\lambda} = \frac{(\Delta E - \lambda)^2}{4\lambda}, \tag{A4}$$

as in Eq. (1).

In the high-temperature activated regime, where $k_BT \gg \hbar\omega/2$, the multiphonon trapping process occurs primarily through $\vec{Q} = \vec{Q}_c$,[21,24] giving Eq. (2), where the off-diagonal matrix element $V(\vec{Q}_c) = \vec{Q}_c \cdot \vec{B}$.[24,46] The case of the low temperature tunneling regime will be discussed at the end of this Appendix.

b. Perturbative calculation with IB

We now consider dopants forming an IB. We develop this argument formally using Eq. (A1) in the case with N impurity levels. The A^i are now matrices that couple IB states. In the basis of localized IB states, the $A^i_{\alpha\beta}$ should be local matrices, either diagonal or with small off-diagonal components, as the phonons mainly act to raise and lower the energy of occupying a given localized state; off-diagonal terms in this basis encourage delocalization, which is not expected for phonons. The calculation below is simplest if we assume that the A^i are all diagonal in the localized basis (or otherwise that they all commute), but we will keep their off-diagonal components and formally treat them as small.

First consider $h = 0$. As in the variational argument, there is a vector $\vec{Q}_0$ such that the largest eigenvalue of

$$H_0 = \vec{Q}_0 \cdot \vec{A} \tag{A5}$$

is $\Delta E'$ and $\sum_i \omega_i^2 Q_{0,i}^2$ is minimal (also see Ref. 33). Choose the basis $\{\psi_\alpha\}$ for $\alpha = 0 \ldots N-1$ to be the eigenstates of H_0, with eigenvalues $\{E_\alpha\}$ with $E_0 = \Delta E'$. Using the constraint $\Delta E' = \langle \psi_0 | H_0 | \psi_0 \rangle$, we find $\vec{Q}_0$ using a Lagrange multiplier, minimizing

$$f = \frac{1}{2}\sum_i \omega_i^2 Q_{0,i}^2 + l(\Delta E' - \vec{Q}_0 \cdot \vec{A}_{00}), \tag{A6}$$

where we use the notation $A_{\alpha\beta} \equiv \langle \psi_\alpha | A | \psi_\beta \rangle$, giving

$$Q_{0,i} = \frac{\Delta E'}{2\lambda_0} \frac{A_{00}^i}{\omega_i^2}, \tag{A7}$$

and we define the isolated impurity relaxation energy

$$\lambda_0 = \sum_i \frac{(A_{00}^i)^2}{2\omega_i^2}. \tag{A8}$$

Together, these give the activation energy

$$E_a^0 = \frac{1}{2}\sum_i \omega_i^2 Q_{0,i}^2 = \frac{(\Delta E')^2}{4\lambda_0}, \tag{A9}$$

just as in Eq. (1).

When we include h, we want to find a vector $\vec{Q}$ such that the highest eigenvalue of the Hamiltonian

$$\tilde{H}(\vec{Q}) = h + \vec{Q} \cdot \vec{A} \tag{A10}$$

is equal to $\Delta E'$, and E_a is minimal. Let the highest eigenvalue of $\tilde{H}(\vec{Q})$ be $\tilde{E}_0(\vec{Q})$.

When we include h, we must also consider a shift in the phonon vector,

$$\vec{Q} = \vec{Q}_0 + \Delta\vec{Q}. \tag{A11}$$

We consider the perturbation Hamiltonian

$$H_1 = h + \Delta\vec{Q} \cdot \vec{A}, \tag{A12}$$

and we seek the self-consistent solution $\Delta\vec{Q}$ such that the highest eigenvalue of $\tilde{H} = H_0 + H_1$ is $\Delta E'$ and $\sum_i \omega_i^2 Q_i^2/2$ is minimal.

We consider second-order perturbation theory. Near the configuration $\vec{Q}_0$, the electron-phonon coupling most strongly perturbs a single localized state, so we can assume that no $E_{\alpha>0}$ is close to degenerate with E_0. When H_1 is added, the highest eigenvalue is

$$\tilde{E}_0 = E_0 + \langle \psi_0 | H_1 | \psi_0 \rangle + \sum_{\alpha>0} \frac{|\langle \psi_\alpha | H_1 | \psi_0 \rangle|^2}{E_0 - E_\alpha} + \text{third order}. \tag{A13}$$

We impose the constraint that $\tilde{E}_0 = E_0 = \Delta E'$ by minimizing the function

$$f = \sum_i \frac{1}{2}\omega_i^2 (Q_{0,i} + \Delta Q_i)^2 + l(\tilde{E}_0 - E_0). \tag{A14}$$

$$\frac{\partial f}{\partial \Delta Q_i} = 0 = \omega_i^2 (Q_{0,i} + \Delta Q_i) + l\left[A_{00}^i + 2\sum_{\alpha>0} \frac{h_{\alpha0} + \Delta\vec{Q} \cdot \vec{A}_{\alpha0}}{E_0 - E_\alpha} A_{\alpha0}^i\right], \tag{A15}$$

where we have assumed that all the wavefunctions and operators are real.

If the matrices A^i all commute, then $A_{\alpha0}^i \propto \delta_{\alpha0}$. We instead assume that the $A_{\alpha0}^i$ are small for $\alpha > 0$ and consider h and $\sum_{\alpha>0} \vec{Q}_c \cdot \vec{A}_{\alpha0}$ to be of the same order. Then the term $\Delta\vec{Q} \cdot \vec{A}_{\alpha0} A_{\alpha0}^i$ in Eq. (A15) is third order and can be neglected. Note that since the $|\psi_\alpha\rangle$ are eigenstates of $\vec{Q}_0 \cdot \vec{A}$,

$$\vec{Q}_0 \cdot \vec{A}_{\alpha0} = \delta_{\alpha0} \Delta E'. \tag{A16}$$

Using this result and Eq. (A7),

$$\sum_i A_{\alpha0}^i \frac{A_{00}^i}{\omega_i^2} = \sum_i A_{\alpha0}^i Q_{0,i} \frac{2\lambda_0}{\Delta E'} = 2\lambda_0 \delta_{\alpha0}. \tag{A17}$$

Then we find

$$l = \frac{-\Delta E' + h_{00} + \sum_{\alpha>0} \frac{|h_{\alpha0}|^2}{E_0 - E_\alpha}}{2\lambda_0} \quad \text{and}$$
$$\Delta Q_i = -\left(h_{00} + \sum_{\alpha>0} \frac{|h_{\alpha0}|^2}{E_0 - E_\alpha}\right) \frac{Q_{0,i}}{\Delta E'} - \frac{\Delta E'}{\lambda_0 \omega_i^2} \sum_{\alpha>0} \frac{h_{\alpha0} A_{\alpha0}^i}{E_0 - E_\alpha}. \tag{A18}$$

Note that the first term of $\Delta\vec{Q}$ is parallel to $\vec{Q}_0$. The last term of $\Delta\vec{Q}$ shifts the direction of the phonon coordinates and is second order (or zero if the A^i commute).

We use this result and Eq. (A7) to find the new activation energy, Eq. (4), which is obtained by keeping terms to second order and again using Eq. (A16). Note that the shift in the direction of the lattice distortion has no effect on E_a, at least to second order.

3. Valence band trapping

A similar estimate can be made for the IB to VB trapping process: trapping occurs through the phonon coordinate $\vec{Q}_v$ such that the lowest energy filled IB state is degenerate with a VB state. The relevant Hamiltonian is the same as in Eq. (A1), with the addition of a term $\varepsilon_V |\phi_v\rangle\langle\phi_v|$, with $|\phi_v\rangle$ a VB state, where $\varepsilon_V = \varepsilon_C - E_g$. We define the energy gap between the filled impurity state and the VB to be $\Delta E_v = \varepsilon_0 - \varepsilon_V$. Then the activation energy to first order is

$$E_{a,v} = \frac{(\Delta E_v - \lambda_0 - h_{00})^2}{4\lambda_0}. \tag{A19}$$

Note that the unperturbed phonon coordinate, as in Eq. (A7), is

$$\vec{Q}_{0,v} = -\frac{\Delta E'_v}{2\lambda_0}\frac{\vec{A}_{00}}{\omega_i^2} = -\frac{\Delta E'_v}{\Delta E'}\vec{Q}_0, \tag{A20}$$

where $\Delta E'_v = \Delta E_v + \lambda_0$. We see that $\vec{Q}_{0,v}$ is a displacement of the opposite sign from $\vec{Q}_0$ but in the same direction.

Note that if h_{00} is close to ε_2, as in Eq. (5), the CB trapping rate is slowed, but the VB trapping rate is increased, and vice versa if h_{00} is close to ε_1. The overall recombination rate will be minimized by slowing whichever of the CB and VB trapping rates is rate-limiting. For a functioning IB photovoltaic, both trapping rates must independently be small, so the material can sustain separate quasi-Fermi levels for the CB, IB, and VB populations,[2] as in Fig. 1.

4. Partially filled IB

We now consider the case of an IB that is not initially empty. If the IB bandwidth is less than λ_0, then small-polaron formation[47] will localize the filled IB states, splitting the IB into a lower-energy, filled band and a higher-energy empty IB, which should behave as described in this paper. If the IB bandwidth is significantly greater than λ_0 and if the IB begins partially occupied, the effective gap to the CB, $\Delta E'$, of Eq. (1) will be increased if the localized state $|\psi_0\rangle$ begins partially occupied. An energy cost of up to λ_0 must be paid to empty the state, which will decrease the trapping rate.

5. Highly mismatched alloys

While we have discussed dopant-produced IB's, a similar result holds for HMA, in which the IB is formed by the repulsion of the CB from resonances above the CB minimum.[5,48,49] In this case, recombination can still proceed through the IB, but there is no isolated impurity state for comparison. Multiphonon trapping will still occur through the localized states in the IB, since they are the eigenstates of the electron-phonon coupling. For any IB, the reorganization energy λ_0 is determined by the smallest wavefunction that can be made by linear combinations of the states of the IB.[50] In addition to this λ_0, the HMA IB can still be characterized by a maximum and minimum energy ε_1 and ε_2 and bandwidth $J = \varepsilon_1 - \varepsilon_2$. As long as $J \ll \varepsilon_C - \varepsilon_1$, the localized wavefunctions will become approximate eigenstates of the IB as the lattice is distorted, and multiphonon trapping through the localized states will occur, as described above for the dopant-produced IB. Since the IB in the HMA case forms from the undoped CB, λ_0 may be considerably smaller than in the deep-level-dopant case, giving a small multiphonon recombination rate; nontrivial lifetime recovery is still not expected.

6. Low-temperature limit

The high-temperature limit used in Eq. (2) is only applicable for $k_BT \gg \hbar\langle\omega\rangle$, where $\langle\omega\rangle$ is the typical phonon frequency. At low temperatures, the phonon momentum must be treated correctly, and tunneling is required to realize the multiphonon trapping process. In the low-temperature tunneling regime

$$\gamma \propto \exp\left\{-\frac{\Delta E}{\hbar\omega_M}\left[\log\left(\frac{\Delta E}{\lambda}\right) - 1\right]\right\}, \tag{A21}$$

where ω_M is the maximum phonon frequency.[51] The effect of h is effectively to change ΔE without changing λ (see Eq. (A2)). With a deep IB, $\Delta E \gg \lambda$ so $\Delta E \approx \sqrt{4\lambda E_a}$. In this case, γ still decreases exponentially with $\sqrt{E_a}$, and the above analysis of the qualitative effect of delocalized states is still valid.

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