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Comment on “Comparative study of *ab initio* nonradiative recombination rate calculations under different formalisms”

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In a recent paper¹ Shi, Xu, and Wang (SXW) compare several formalisms to calculate nonradiative recombination rates due to multiphonon emission. SXW use the $\text{Zn}_{\text{Ga}}\text{-O}_{\text{P}}$ center in GaP as a benchmark to compare calculations of the electron capture cross section, σ_n , to available experimental data. Included in the set of formalisms is the “one-dimensional (1D) quantum formula” which was used recently by Alkauskas *et al.* in *ab initio* calculations of nonradiative capture rates² [*cf.* Eq. (36) of Ref. 1 and Eq. (22) of Ref. 2].

SXW first show that the so-called adiabatic approximation is not appropriate to describe carrier capture, which is in agreement with the conclusions of Ref. 2. SXW then demonstrate that all other formalisms lead to values of σ_n that are very comparable—except for the 1D quantum formula. The 1D quantum formula calculations reported by SXW yield significantly lower values of σ_n and, in addition, exhibit a very different temperature dependence. SXW conclude that the use of an effective single phonon mode that is employed in the 1D quantum formula is insufficient to quantitatively describe nonradiative capture rates and their temperature dependence.

We have performed a detailed analysis of the SXW results and find that the parameters they use in the 1D quantum formula are internally inconsistent, pointing to an error in their approach. In this Comment we demonstrate that a correct application of the 1D quantum formula provides results that are accurate and reliable.

The 1D quantum formula approach can be explained by the configuration coordinate diagram³ illustrated in Fig. 1. If we consider the capture of an electron by an acceptor defect, the excited state of the system corresponds to the acceptor in the neutral charge state and an electron in the conduction band ($A^0 + e^-$), while the ground state corresponds to the negative charge state of the acceptor (A^-). The curvature of the two parabolas is determined by the vibrational frequency $\hbar\Omega_j$, which is assumed to be the same for the excited state and the ground state. In the harmonic approximation one can show that the barrier for a nonradiative transition is $\Delta E_b = \frac{(\Delta E_{ij} - \lambda)^2}{4\lambda}$. The horizontal displacement between the two parabolas represents the change in the atomic geometry of the defect following the change in charge state induced by carrier capture.

In Table I of their study,¹ SXW outline the parameters used in their 1D quantum formula calculation for $\text{Zn}_{\text{Ga}}\text{-O}_{\text{P}}$ in GaP. The vibrational frequency $\hbar\Omega_j=5.38$

FIG. 1. One-dimensional configuration coordinate diagram for electron capture at the $\text{Zn}_{\text{Ga}}\text{-O}_{\text{P}}$ defect in GaP using (a) values for $\hbar\Omega_j$, ΔQ and ΔE_{ij} listed in Table I of SXW (Ref. 1) and (b) parameters from our own calculations. The defect in its neutral charge state captures an electron and becomes negative. ΔE_b is the classical barrier for nonradiative capture, as described in the text. λ is the relaxation energy in the ground state of the system.

meV and Huang-Rhys factor $S=12.61$ quoted in the table should lead to a relaxation energy λ of $S\hbar\Omega_j=67.8$ meV [see Fig. 1(a)]. However, the value for λ listed by SXW is 190 meV. This error calls into question the values for σ_n calculated using the 1D quantum formula by SXW, and the validity of the conclusions drawn from these results.

To address these discrepancies we conducted our own calculations for $\text{Zn}_{\text{Ga}}\text{-O}_{\text{P}}$ in GaP following the same approach as described by SXW.¹ The density functional theory calculations use the Vienna Ab-initio Simulation Package (VASP).^{4,5} The generalized gradient approximation (GGA) was used for all atomic relaxations. Based on the atomic structure obtained with GGA, the electronic structure was calculated using the hybrid functional of Heyd, Scuseria and Ernzerhof,⁶ with a mixing parameter set to 0.2. The plane-wave energy cutoff was 400 eV. Point-defect calculations were performed using a 64-atom supercell and the Brillouin zone was sampled using a $2\times 2\times 2$ Monkhorst-Pack k -point grid. Electron capture coefficients are computed from first principles following the methodology described in Ref. 2. **The electron-phonon matrix elements were calculated by Taylor expanding around the geometry of the final charge state, as in Refs. 1 and 2. We also used a degeneracy factor of $g=4$ to represent the degeneracy of the final state in the capture process**

	SXW	Present study
W_{ij} (meV/amu ^{1/2} Å)	2.5	3.1
ΔQ (amu ^{1/2} Å)	4.43	4.68
ΔE_{ij} (eV)	0.282	0.253
$\hbar\Omega_j$ (meV)	5.38	9.51
S	12.61	24.07
λ (eV)	0.19	0.23

TABLE I. Key parameters for the 1D model of the $\text{Zn}_{\text{Ga}}\text{-O}_{\text{P}}$ center in GaP. W_{ij} is the electron-phonon matrix element, ΔQ is the total mass-weighted distortion (see Fig. 1), and ΔE_{ij} is the ionization energy. $\hbar\Omega_j$ is the vibrational frequency, S_j the Huang-Rhys factor, and λ the relaxation energy, all for the ground state. The results of SXW¹ are compared with results of our present calculations.

so as to be consistent with the choice made by SXW.¹

Figure 1(a) illustrates the results reported by SXW¹ and Fig. 1(b) the results of our own calculations. All the relevant parameters are listed in Table I. The comparison in Table I shows that our calculated vibrational frequency $\hbar\Omega_j$ is larger than the results of SXW by a factor 1.77, as is also evident from the difference in curvature of the curves in Fig. 1.

Using the parameters from our calculations listed in Table I we calculate the temperature-dependent electron capture coefficient, C_n , and then obtain a capture cross section, σ_n , using the relation $C = \sigma_n \langle v \rangle$. The thermal velocity $\langle v \rangle$ for electrons in GaP is set to the root-mean-square velocity $\sqrt{3k_B T/m_e}$, where m_e is the electron effective mass, k_B is the Boltzmann constant, and T the temperature. The results are plotted in Fig. 2 and compared with the SXW results.

The comparison allows us to draw several conclusions. First, the 1D quantum formula results of SXW¹ (“SXW-1D” in Fig. 2) differ significantly (by up to several orders of magnitude) from the values obtained in the present work. The SXW values exhibit a strong temperature dependence that is markedly different from the present calculations. These discrepancies can be traced to an error made by SXW in extracting parameters for their implementation of the 1D quantum formula. If one uses the values of W_{ij} , ΔQ , ΔE_{ij} as reported in Table I of SXW¹ (and reproduced in our Table I), and would extract $\hbar\Omega_j$ from λ , also reported in Table I of SXW, one would obtain σ_n not too different from our present results shown in Fig. 2. However, SXW appear to have made an error in extracting the value of $\hbar\Omega_j$. The use of an erroneous value of $\hbar\Omega_j$ leads to the values of σ_n shown in Fig. 8 of SXW¹ (and reproduced in our Fig. 2, “SXW-1D”). We note that the parameters of SXW give rise to a sizeable value for the classical barrier $\Delta E_b = 169$ meV [Fig. 1(a)], which in turn leads to a strong temperature dependence and significantly lower values of σ_n when compared to the other formalisms studied in Ref. [1]. In contrast, using the parameters from our own calculations (Table I) we

FIG. 2. (Color online) Electron capture cross section at the $\text{Zn}_{\text{Ga}}\text{-O}_{\text{P}}$ center in GaP. Results for the 1D quantum formula obtained in the present study are indicated with a black solid line (“Present study”). Results for the 1D quantum formula reported by SXW (Fig. 8 in Ref. 1) are indicated by orange diamonds (“SXW-1D”). For comparison, results for the quantum charge transfer formalism as reported by SXW are also included (blue inverted triangles, “SXW-QCT”).

obtain a very small value for ΔE_b (~ 0.5 meV). This low classical barrier is consistent with the weak temperature dependence observed in our calculation of σ_n (Fig. 2).

Our calculated values of σ_n and their temperature dependence (Fig. 2) are in good agreement with the “static coupling” results of SXW that include the contributions of all phonons. They are in even better agreement with the results from a quantum charge transfer (QCT) formalism, which is a quantum-mechanical extension of classical Marcus theory.

Our calculated results are larger by only up to a factor of 2 across a temperature range of 0 K to 450 K when compared to the QCT results, while for the temperature range of 450 K to 1000 K they are slightly lower compared to the QCT results by SXW. **At 150K, our value of σ_n is $6.8 \times 10^{-15} \text{ cm}^2$, compared to a value of $3.0 \times 10^{-15} \text{ cm}^2$ from the QCT calculations by SXW. At 1000 K, our σ_n value is $1.6 \times 10^{-15} \text{ cm}^2$, compared to $2.6 \times 10^{-15} \text{ cm}^2$ from the QCT calculations by SXW.**

In conclusion, our calculations for $\text{Zn}_{\text{Ga}}\text{-O}_{\text{P}}$ in GaP show that the 1D quantum formula formalism that relies on a single effective phonon mode yields results for capture cross sections that are close to those obtained by SXW using either the QCT or the static coupling formalism.¹ We find the conclusions drawn by SXW regarding the inaccuracy of the 1D quantum formula formalism to be unfounded, and based on an error in extracting the relevant parameters.

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