Auger recombination in sodium-iodide scintillators from first principles
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Auger recombination rates in nitrides from first principles
Scintillator devices based on sodium iodide (NaI) are used in national security to enable simple and fast scanning for radioactive materials in shipping containers at ports or on trucks. Scintillators convert high-energy gamma rays into photons of lower energy [Fig. 1(a)] that are easier to analyze using optoelectronic devices. The goal of this analysis is to identify the elemental source of detected gamma radiation. Unfortunately, current scintillator materials including NaI suffer from low energy resolution that leads to high false-alarm rates for materials such as ceramics or cat litter that are not considered a severe threat.\(^1,2\) These false-positives can be offset by additional instrumentation, which, however, leads to increased cost and complexity of the scanning system. Many recent studies investigated the non-proportionality effect in order to improve the accuracy of scintillator detectors (Refs. 3–11).

One dissipative process that may play a role in scintillator non-proportionality is Auger recombination (AR). Direct AR takes place when an electron and hole recombine non-radiatively to excite a third carrier instead of radiating a photon [Figs. 1(b) and 1(c)]. Indirect AR occurs when the non-radiative recombination process is assisted by a carrier-scattering mechanism that provides additional momentum, e.g., a phonon [Fig. 1(d)]. The total AR rate \(R_{\text{Auger}}\) is proportional to the third power of the free-carrier density \(n\), and the Auger coefficient \(C\) is defined as \(R_{\text{Auger}} = Cn^3\) (Ref. 12). A comparison with the radiative recombination rate, which increases with the square of the free-carrier density, \(R_{\text{rad}} = Bn^2\), shows that AR dominates at high carrier densities. AR is thought to reduce the high-power efficiency of light emitting diodes,\(^13,14\) and also may play an instrumental role in the non-proportionality problem of scintillators.\(^11,15–17\) In all of these cases, understanding the microscopic mechanism of AR is a prerequisite to improving the device performance.

There is no theoretical and very little experimental data regarding AR in NaI. Experimental measurements of AR in scintillators are extremely difficult, since each incident gamma-ray photon generates multiple carriers, which can interact through several non-radiative mechanisms that are impossible to discern directly. The analysis of experimental data must then try to relate properties such as the light yield to models that include AR rate parameters. However, different experimental conditions and underlying assumptions used in models can lead to seemingly different AR coefficients spanning many orders of magnitude. Using rate equations for the temporal and spatial evolution of excitation densities, the work in Ref. 8 found an AR coefficient of \(1.07 \times 10^{-20} \text{ cm}^2 \text{s}^{-1}\) when modeling Compton coincidence data from SLYNCI (see Ref. 5). On the other hand, a much smaller coefficient of \(3.2 \times 10^{-29} \text{ cm}^6 \text{s}^{-1}\) was reported when modeling z-scan experiments using a pulsed laser.\(^16,17\)

![FIG. 1. Schematic illustration of recombination processes in scintillators after a high-energy impact. (a) Radiative recombination of an electron-hole pair produces a photon. (b) and (c) In non-radiative Auger recombination, the energy of the recombining pair is transferred to a third carrier, either (b) an electron (e-e-h Auger) or (c) a hole (h-h-e Auger) that gets excited to a higher energy state. (d) Auger recombination can also be mediated by a phonon.](http://dx.doi.org/10.1063/1.4914500)
These few data points span nine orders of magnitude and emphasize the need for first-principles studies of AR in scintillators to thoroughly understand the involved processes and provide complementary and independent insight without empirical assumptions.

In this work, we investigate direct and phonon-assisted AR in sodium iodide, a widely used and well characterized scintillating material, using first-principles calculations based on density functional theory (DFT). We show that AR is dominated by the phonon-assisted process at room temperature and is primarily mediated by short-range acoustic and longitudinal optical (LO) phonons. From our computations, we derive values of $1.15 \pm 0.01 \times 10^{-32} \text{cm}^6 \text{s}^{-1}$ for the direct and $5.6 \pm 0.3 \times 10^{-32} \text{cm}^6 \text{s}^{-1}$ for the phonon-assisted AR coefficient. Our analysis shows that direct AR follows an Arrhenius activation law and exceeds the phonon-assisted AR rate at electronic temperatures higher than $1360 \text{K}$.

Our computational methodology is based on DFT in the generalized-gradient approximation and the plane-wave norm-conserving pseudopotential method. The calculated electronic structure of NaI is shown in Fig. 2. The gap has been rigidly adjusted to the experimental value $E_g = 5.8 \text{eV}$ to account for the band-gap problem of DFT. Spin-orbit interaction effects were not included in the calculations. The maximally localized Wannier function method was used to interpolate the energy bands to fine grids in the first Brillouin zone (BZ). Direct and phonon-assisted AR rates were calculated as described in Refs. 13, 25, and 26. Gaussian functions with a width of 0.1 eV were used to evaluate the energy delta functions for the AR rates. We used a model dielectric function to calculate the screened Coulomb interaction matrix elements, including the screening by free carriers using the Debye-Hückel equation for non-degenerate carriers and the Thomas-Fermi model for degenerate carrier concentrations. The lattice temperature is set to be 300 K, while the electron temperature is set to be 500 K. We assume a carrier density of $10^{19} \text{cm}^{-3}$. We use a relaxed lattice constant of 12.58 Bohr radii and the experimental high frequency dielectric constant $\varepsilon_\infty = 2.98$ (Ref. 28).

Figure 2 shows the calculated band structure of NaI. AR excites carriers to states that are at energies approximately equal to the band gap from the conduction and valence-band edges. As is evident from the band structure in Fig. 2, there are numerous conduction bands at the energy $(2E_g = 11.6 \text{eV})$ needed to accommodate hot electrons excited by the e-e-h Auger process [Fig. 1(b)]. Thus, we conclude that direct and phonon-assisted e-e-h AR are possible in NaI. However, there are no valence-band states around $-5.8 \text{eV}$ to accommodate holes excited by the h-h-e Auger process [Fig. 1(c)] and therefore h-h-e AR cannot occur in NaI. In the following, we focus our attention to e-e-h Auger processes only.

The calculated values for the direct e-e-h AR coefficients are shown in Fig. 3. To estimate the sensitivity of the calculated coefficients to the band gap value, we adjusted the value of the band gap between 4.5 and 6.5 eV. The calculated value at the experimental band gap is $1.15 \pm 0.01 \times 10^{-32} \text{cm}^6 \text{s}^{-1}$.

Figure 3 shows that a BZ sampling grid of $30 \times 30 \times 30$ is sufficient to converge the Auger coefficients. The same figure also shows that the direct Auger coefficient does not depend sensitively on the band gap. For example, if the band gap changes within $\pm 0.3 \text{eV}$ from the experimental value (5.8 eV) the direct Auger coefficient changes by at most 50%. The dependence of the direct Auger coefficient on the band gap follows the Arrhenius activation law derived for intraband Auger processes [$C \propto \exp(-E_A/kBT)$] even though direct AR in NaI occurs through interband processes to higher conduction bands. Here, $E_A$ is the activation energy which is proportional to the band gap. We show below that $E_A = 0.18 \text{eV}$, which is a small fraction (3.1%) of the experimental gap.

The phonon-assisted AR coefficients are shown in Fig. 4 as a function of the band gap. The value of the phonon-assisted Auger coefficient at the experimental band gap, $5.6 \pm 0.3 \times 10^{-32} \text{cm}^6 \text{s}^{-1}$, is approximately a factor of 5 larger than the direct one and therefore phonon-assisted processes dominate AR in NaI. This value is also comparable to phonon-assisted e-e-h AR values in semiconductors such as GaN ($4 \times 10^{-32} \text{cm}^6 \text{s}^{-1}$) and GaAs ($1.1 \times 10^{-31} \text{cm}^6 \text{s}^{-1}$).
Comparing with the coefficients fitted to experimental data, we note that our calculated rate is several orders of magnitudes smaller than the value of $1.07 \times 10^{-20} \text{cm}^6 \text{s}^{-1}$, which is approximately two orders of magnitude larger than the direct Auger coefficient (cf. Fig. 3).

FIG. 5. The contribution of the various phonon modes to the phonon-assisted Auger coefficient of NaI. The phonon-assisted processes are dominated by the acoustic and the LO phonon modes, while the contribution by the TO phonons is approximately one order of magnitude smaller.

results from fits ($C = 3.2 \times 10^{-29} \text{cm}^6 \text{s}^{-1}$) to z-scan experiments, our calculated values are off by a few decades.\(^\text{16,17}\) This illustrates the difficulty in fitting a rate equation model to a very complex set of events and interdependent mechanisms. While one possible cause for the difference between our results and experimental data is thallium doping present in NaI samples that were studied in experiment, we note that Refs. 16 and 17 have considered both pristine and Tl-doped CsI with only a small variation (a factor of about 1.5) of the AR coefficients. We therefore expect that the inclusion of dopants does not have a large effect on the AR rate.

Interestingly, for a wide range of materials, Williams et al., noted an empirical band-gap rule.\(^\text{16,17}\) This trend was however not followed by the halide systems under consideration, which instead displayed values that exceeded the expected values by three to four orders of magnitude. The plausible explanation by the authors was the following: (i) the underlying model and assumptions are wrong or insufficient, or (ii) the excitation energy exceeds the band gap of NaI by about 0.3 eV (3500 K electronic temperature) and might leave the carriers with very high electronic temperatures, or (iii) the Auger recombination might involve self-trapped holes ($V_k$-centers) with localized hole states in the forbidden gap. We note that our predicted value actually obeys the observed empirical band gap rule. To assess the effect of high electronic temperature on AR coefficients, we performed direct AR calculations for increasing electronic temperatures up to 2500 K (Fig. 7). The high-temperature calculations were performed with a $14 \times 14 \times 14 \text{k}$ point grid since the convergence with respect to mesh size is faster for higher temperatures. We further fitted the data for the experimental band gap of 5.8 eV with an Arrhenius activation law $C(T) = C_0 \exp(-E_A/k_B T)$ (inset of Fig. 7). The fit parameters are $C_0 = 2.94 \times 10^{-31} \text{cm}^6 \text{s}^{-1}$ and $E_A = 0.18 \text{eV} = 0.031E_g$. Using this model, we obtained changes in the direct AR coefficient of at most 50% if the band gap is changed by $\pm 0.3$ eV as was found in the calculated data. The Arrhenius model finds that the direct AR rate surpasses the calculated low-temperature phonon-assisted rate for electronic temperatures higher than 1360 K. However, even

FIG. 6. The distribution of the contribution by the various phonon wave vectors to the phonon-assisted Auger coefficient of NaI. The vertical line represents the edge of the BZ.

FIG. 4. Calculated phonon-assisted e-e-h Auger recombination coefficients of NaI as a function of the adjusted band gap and the BZ sampling. The phonon-assisted Auger coefficient at the experimental band gap value is $5.6 \pm 0.3 \times 10^{-32} \text{cm}^6 \text{s}^{-1}$, which is approximately two orders of magnitude larger than the direct Auger coefficient (cf. Fig. 3).
at infinite electronic temperature the maximum direct AR coefficient ($C_0 = 2.94 \times 10^{-31}$ cm$^6$ s$^{-1}$) is still much smaller than experimental results.

The third possibility of a self-trapped hole to participate in the Auger process is indeed very interesting, but it is beyond the scope of the present work. We note however that the localized nature of the hole level relaxes the momentum conservation selection rules and may lead to larger rates. Furthermore, it is also possible that the localized empty levels provide more routes for direct AR.

In summary, we performed first-principles calculations to find the direct and phonon-assisted AR coefficients for the basic scintillating material, sodium iodide. We found that the phonon-assisted process is dominant in NaI at low electronic temperatures, and the magnitude of the AR coefficient is smaller than values derived in the previous work. Understanding AR and resolving the discrepancy with previous modeling work is necessary to successfully model the scintillating process in sodium iodide. Being able to better predict how this and other scintillating materials react during the high-energy impact would allow us to guide future materials design aimed at dramatically improving the device performance and detecting that easily allow radiation sources to be identified without error.

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FIG. 7. The direct Auger recombination coefficient for varying electronic temperatures. The direct AR coefficient follows an Arrhenius activation-law model (inset), which predicts a maximum direct AR coefficient of $2.94 \times 10^{-31}$ cm$^6$ s$^{-1}$ and surpasses the calculated low-temperature phonon-assisted rate for electronic temperatures higher than 1360 K.