

The foundations of Shockley's equation for the average electron-hole-pair creation energy in semiconductors

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ABSTRACT

Energetic carriers in semiconductors thermalize by impact-ionization, which generates electron-hole pairs (EHPs), and by energy losses to phonons. The average EHP creation energy is typically about three times the energy gap. In 1960, Shockley derived a simple equation for the average EHP creation energy with a single free parameter that fits experimental values for a wide range of materials, but the underlying assumptions, as stated, have been widely criticized as lacking justification. Modified expressions derived by improved approximations have been proposed but do not fare better. Here, we revisit the foundations of Shockley's equation and provide a robust justification for the kinetic-energy component as a model averaging procedure and then apply a similar procedure to the phonon component of the equation. The phonon result retains Shockley's form, but the interpretation and justification are now on par with those of the kinetic-energy term. The single-parameter fit to the data remains unchanged, i.e., the present analysis accounts for the exceptional applicability of Shockley's equation.

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Energetic electrons and holes are present in semiconductors and insulators under a variety of experimental conditions, e.g., they are generated by laser, electron, particle-beam, x-ray, or γ -ray irradiation, or during avalanche breakdown in p - n junctions, etc. Such energetic electrons and holes thermalize into free carriers primarily by cascades of impact-ionization events and by energy transfer to phonons between impact-ionization events. Empirically, it has been found that the average energy that is consumed to create a thermalized electron-hole pair (EHP), E_{pair} , is roughly three times the bandgap energy.^{1,2} Shockley addressed the problem back in 1960 as extensive data was accumulating for Si and Ge and used rather bold assumptions to derive a simple equation.^{3,4} The average energy loss per EHP pair is given by

$$E_{pair} = 2.2E_g + rE_R, \quad (1)$$

where E_g is the bandgap, assumed to also be the impact-ionization threshold; E_R is the highest optical-phonon energy; and r is the average number of such phonons that are emitted between EHP

impact-ionization events. The universal coefficient 2.2 in Eq. (1) was actually derived by Shockley. The parameter r is, in principle, a ratio of mean free paths, but it is difficult to measure so that it has generally been treated as a free parameter. The assumptions that Shockley made to derive both the electron and phonon terms in Eq. (1) have been repeatedly criticized as lacking justification and modified expressions derived by improved approximations, have been proposed.^{2,5–11} Such modifications, however, have not fared better. Shockley's equation remains the standard and is highly cited as a single value of r leads to an excellent fit of measured E_{pair} values for a wide range of materials [Shockley's paper has had ~ 900 citations, whereas papers deriving revised versions of Eq. (1) typically have had fewer than 100 citations].

In this Letter, we do not seek to improve Shockley's equation to obtain a better fit to experimental data. Instead, we revisit its derivation and demonstrate that the first term in Eq. (1), which describes the kinetic-energy component of E_{pair} , though it is based on approximations that are not well-justified for any one material, can in fact be recast as the result of a robust model averaging procedure with

universal applicability. We then revisit the second term in Eq. (1) and show that, as originally defined, it is indeed subject to serious scrutiny, especially in the face of recent first-principles calculations of energy dissipation by multiphonon processes¹² and Monte Carlo simulations of electron-thermalization processes in silicon.¹¹ We are able, however, to construct a model averaging procedure for the energy loss to phonons in full analogy with the present recasting of the kinetic-energy component of E_{pair} . The result replaces E_R in Eq. (1) by $0.75\Delta E_{ph}$, where ΔE_{ph} is the energy width of the material's phonon dispersion, which has the same value as Shockley's E_R , but $0.75\Delta E_{ph}$ represents an average phonon energy, compared with the energy of a single phonon mode that Shockley assumed to be dominant. The factor 0.75 can then be absorbed in the fitting parameter r , so that the fit to the data remains intact. Overall, the present analysis accounts for the exceptional applicability of Shockley's equation, which is often viewed as too crude to be good enough.

Shockley's description of the carrier thermalization process is as follows. Energetic carriers generate EHPs by impact ionization with a threshold equal to E_g and excess kinetic energy equal to $E(\mathbf{k})$, namely, some energy in the respective energy bands, up to a maximum absolute value equal to E_g [if the excess kinetic energy were to exceed $2E(\mathbf{k})$, another impact-ionization event would follow]. Shockley then calculates the average excess kinetic energy E_{el} by assuming that the generated carriers "are equally likely to be anywhere in the Brillouin zone with energy less than E_g " and further assuming "parabolic energy surfaces," i.e., of the form $E(\mathbf{k}) = Ak^2$. Based on these assumptions, E_{el} is calculated as follows:

$$E_{el} = \frac{1}{\frac{4}{3}\pi\left(\frac{E_g}{A}\right)^{3/2}} \int_0^{\sqrt{E_g/A}} Ak^2 d^3k = 0.6E_g. \quad (2)$$

An alternative calculation² recognizes that the density of available energies has the form $C\sqrt{E}$, where C is a function of the density-of-states effective mass. Then,

$$E_{el} = \frac{1}{\int_0^{E_g} \sqrt{E} dE} \int_0^{E_g} E\sqrt{E} dE = 0.6E_g. \quad (3)$$

The average energy cost per created EHP is then equal to $E_g + 2E_{el} = 2.2E_g$ as in Eq. (1) (the factor 2 is to account for an electron and a hole).

The assumptions that lead to Eqs. (2) and (3) can be viewed as too crude, even unrealistic for the following reasons:

- The impact-ionization threshold may be larger than E_g for several reasons, e.g., to satisfy momentum conservation.⁶
- The complexity and variation of the energy bands in different materials, even the marked differences between valence and conduction-band dispersions, which serve as initial and final states in impact-ionization processes, make it unlikely that all available energies in the Brillouin zone smaller than E_g are equally populated.
- Assuming a single parabolic energy band $E(\mathbf{k}) = Ak^2$ for both conduction and valence bands for all materials is unrealistic.

It is indeed true that, if we view Shockley's assumptions as approximations, they do lack satisfactory justification. We can,

however, recast them as a model with universal applicability whose validity is ultimately judged by its success in fitting the data with predictive power. In search of a universal model that seeks to capture the essential features of the thermalization process, we posit that details of the energy bands and Brillouin zones can be neglected according to the following internally consistent statements:

- The energy gap E_g can serve as the model's impact-ionization threshold by positing that momentum is conserved on average.
- Since the energy of carriers in the conduction and valence bands is a form of kinetic energy, as in semiclassical treatments of the Boltzmann equation,¹¹ we write the model's excess kinetic energy of impact-ionization-generated carriers in the generic form $p^2/2m$, with values ranging from 0 to E_g . The value of m is, in principle, allowed to depend on the material, encapsulating the diversity of each material's energy bands, but m actually drops out of the average excess kinetic energy (see below).
- We posit that, on average, all the $p^2/2m$ -values arise with equal probability, i.e., fluctuations about the average value can be neglected.

The calculation of the average excess kinetic energy E_{el} is then identical to that of Eqs. (2) and (3). A key point is that the result is independent of m , i.e., the model parameter that generically encapsulates the complexity of energy bands of different materials drops out, signaling a level of robustness for the generic model averaging procedure and universal applicability. Only the energy gap is left as a single identifying parameter for each material.

The above recasting of Shockley's derivation of the electron-kinetic-energy component of E_{pair} [the first term of Eq. (1)] has a number of consequences regarding possible improvements of the model. For example, Klein⁶ has advocated that, for various reasons, it would be "more appropriate" to use $1.5E_g$ for impact-ionization threshold instead of E_g . One such reason is the need to conserve momentum as well as energy. To properly treat momentum conservation, however, one must consider differences between direct- and indirect-gap materials. In the recast model derivation, on the other hand, we forego energy bands and Brillouin zones, retaining only the bandgap as the single material identifier. Momentum conservation is assumed to be satisfied on average.

We now turn to the average energy that is transferred to phonons between impact-ionization events. Shockley posited that "it is probable that the dominant scattering by phonons involves the phonons of highest energy."⁴ He then wrote the phonon contribution as rE_R , where E_R is the highest phonon energy, typically the energy of a Raman-active mode. He offered possible ways to calculate the parameter r for Si and Ge, but r later became a free parameter to fit data for several materials.⁶

In 2015, first-principles calculations found that one must include up to 13 different phonon modes to get a converged value of multiphonon energy dissipation¹² in contrast to prior work that assumed that a single representative phonon mode is adequate. In a more recent paper, Fang *et al.*¹¹ reported full-band, Monte Carlo, Boltzmann-equation simulations of the thermalization of energetic electrons in Si using full electron and phonon dispersions and found that, for complete thermalization, there are more acoustic-phonon than

optical-phonon scattering events, but, because acoustic phonons have relatively small energies, the net energy transfer to phonons is roughly 70% to optical phonons and 30% to acoustic phonons. Such simulations have not been reported for other materials, but the result is likely to vary. We note that, while Si has three optical and three acoustic branches, materials with multiatomic unit cells still have only three acoustic branches, while the number of optical branches can be very large. For example, β -Ga₂O₃, a currently actively researched wide-gap semiconductor, has ten atoms in the primitive unit cell and, therefore, 27 optical phonon branches.¹³ The net conclusion for our purposes is that, as was the case of the excess electron kinetic energies, all phonon modes participate with potentially enormous complexity. We will, therefore, construct a generic model for energy transfer to vibrations parallel to the one just discussed for the excess kinetic energy of EHPs. Thus, on average, we will forego details of the phonon energy bands and Brillouin zones and posit that all phonon modes are excited with equal probability.

Following the logic of the electron model, we start by deriving a generic form of the dependence of the phonon energy on crystal momentum q , analog of $p^2/2m$, generic form of the carrier kinetic energies. The momentum dependence (dispersion) of the phonons of a linear chain of atoms is essentially a straight line, as shown in Fig. 1(a), except for a slight bend as q approaches the Brillouin-zone edge in order to have zero slope at the edge. The straight line for the acoustic mode is known as the Debye approximation. If we double the size of the unit cell to contain two atoms, the Brillouin zone is halved and the dispersion looks as the red line in Fig. 1(b). If the two atoms are not identical, a gap opens up as shown by dashed lines in Fig. 1(b), separating the acoustic and optical modes. We can generalize this construction to a multi-atom unit cell and envision the phonon dispersion as simply a straight line in an extended-zone scheme. When this straight line is folded several times, it produces the pertinent number of optical branches in the first Brillouin zone. As in the case of electrons, however, we forego Brillouin zones and detailed dispersions and adopt a universal isotropic dispersion relation of the form $E(q) = Bq$, ranging up to the highest phonon energy, E_R . We make no distinction between optical and acoustic phonons. This simple expression for phonon energies is the analog of $p^2/2m$ for the carrier kinetic energies. As in the case of the generic electron mass m , the constant B in $E(q) = Bq$ is not to be related to the speed of sound of each material, but it is to be viewed as encapsulating the entire phonon system. Furthermore, we again assume equal probability for the emission of all model phonons with energies $E(q) = Bq$. In three dimensions, following Eq. (2), the average energy E_{ph} dissipated per phonon emission is given by

$$E_{ph} = \frac{1}{\frac{4}{3}\pi(E_R/B)^3} \int_0^{E_R/B} Bkd^3k = 0.75E_R. \quad (4)$$

The same result can be obtained using the density of phonon states arising from the dispersion $E(q) = Bq$. Once more, just like the mass parameter m for electrons and holes, the parameter B drops out so that the result represents a generic average energy with universal applicability, with the material identified only by its phonon bandwidth. The final result for E_{pair} can then be written as

$$E_{pair} = 2.2E_g + r'(0.75E_R) = 2.2E_g + rE_R, \quad (5)$$

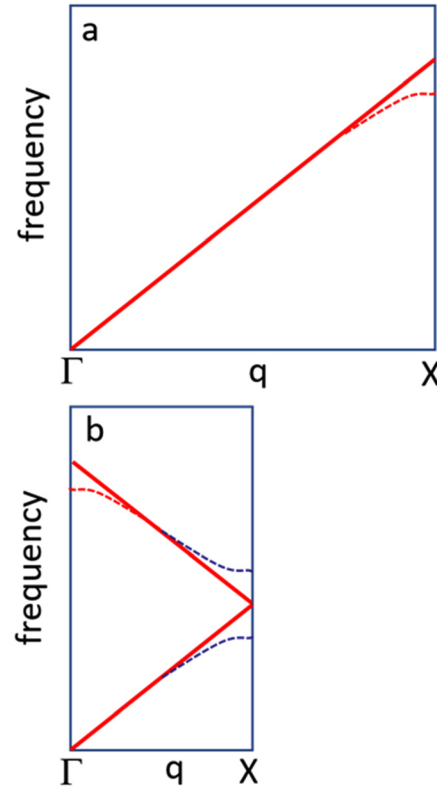


FIG. 1. Model dispersion of phonons for (a) one atom per unit cell and (b) two atoms per unit cell. If the atoms are dissimilar, a gap opens between acoustic and optical phonons. The red dashed lines indicate a more accurate representation. The blue dashed lines indicate the opening of a gap when the two atoms are dissimilar. The solid line in (a) is used to define the present model, $E(q) = Bq$, in an extended-zone scheme, making no distinction between acoustic and optical phonons.

where r' stands for the number of “average phonons” emitted between impact-ionization events. A key point here is the difference of the present model from Shockley’s approximation that emission of the highest-energy phonons dominates the energy transfer. Here, $0.75E_R$ is a model universal average phonon energy applicable to any material. We note that the final form is identical to Shockley’s equation, Eq. (1), with $r = 0.75r'$, but, in principle, E_R now does not stand for the energy of a particular phonon but for the energy width of the phonon dispersion. Nevertheless, there is no change in the process of fitting data to obtain a universal value of r . The only difference between Eqs. (5) and (1) is that Eq. (5) is derived using the same type of universal model for both electrons and phonons. Note that, in Eq. (5), the electron term depends only on the bandgap E_g and the phonon term depends only on the phonon-dispersion energy width E_R . The validity of the model is confirmed by the fact that a universal r fits the measured E_{pair} values of a wide range of materials.

In summary, we have demonstrated that, though Shockley’s original equation was derived using approximations whose validity is highly questionable, we recast the formula by constructing universal averaging models for both the electron and phonon components of the formula. The validity of the model is confirmed by the fact that

Eq. (5), being equivalent to Shockley's equation (1), exhibits an excellent fit to the measured E_{pair} values of a wide range of materials with a universal r value. The generic treatments of the electron and phonon energies, both of which forego Brillouin zones and details of the electron and phonon bands, leave no room for slight modifications to improve the predictive power.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

REFERENCES

- ¹F. Lappe, "The energy of electron-hole pair formation by x-rays in PbO," *J. Phys. Chem. Sol.* **20**, 173–176 (1961).
- ²R. C. Alig and S. Bloom, "Electron-hole-pair creation energies in semiconductors," *Phys. Rev. Lett.* **35**, 1522 (1975).
- ³W. Shockley, "Problems related to pn junctions in silicon," *Czech. J. Phys.* **11**, 81–121 (1961).
- ⁴W. Shockley, "Problems related to pn junctions in silicon," *Solid-State Electron.* **2**, 35 (1961).
- ⁵E. Antončík, "Impact ionization and quantum efficiency in semiconductors," *Czech. J. Phys. B* **17**, 953–968 (1967).
- ⁶C. A. Klein, "Bandgap dependence and related features of radiation ionization energies in semiconductors," *J. Appl. Phys.* **39**, 2029–2038 (1968).
- ⁷W. Czaja, "Zur theorie der arbeit pro elektron-loch-paar in halbleitern de IV gruppe," *Helv. Phys. Acta* **34**, 760 (1961).
- ⁸F. E. Emery, *The Average Energy Expended per Ionized Electron-Hole Pair in Semiconductors* (Rice University, 1965).
- ⁹R. C. Alig, S. Bloom, and C. W. Struck, "Scattering by ionization and phonon emission in semiconductors," *Phys. Rev. B* **22**, 5565 (1980).
- ¹⁰R. C. Alig, "Scattering by ionization and phonon emission in semiconductors. II. Monte Carlo calculations," *Phys. Rev. B* **27**, 968 (1983).
- ¹¹J. Fang, M. Reaz, S. L. Weeden-Wright, R. D. Schrimpf, R. A. Reed, R. A. Weller, M. V. Fischetti, and S. T. Pantelides, "Understanding the average electron-hole pair-creation energy in silicon and germanium based on full-band Monte Carlo simulations," *IEEE Trans. Nucl. Sci.* **66**, 444–451 (2019).
- ¹²G. D. Barmparis, Y. S. Puzyrev, X.-G. Zhang, and S. T. Pantelides, "Theory of inelastic multiphonon scattering and carrier capture by defects in semiconductors: Application to capture cross sections," *Phys. Rev. B* **92**, 214111 (2015).
- ¹³A. Parisini, K. Ghosh, U. Singiseti, and R. Fornari, "Assessment of phonon scattering-related mobility in β -Ga₂O₃," *Semicond. Sci. Technol.* **33**, 105008 (2018).