

been studied recently by J. S. Jayson and R. Z. Bachrach [Phys. Rev. B **4**, 477 (1971)], who attribute the 2.2-eV band to pair recombination at either Si or S donors. They deduce a capture cross section for the donor of 5×10^{-14} – 5×10^{-13} cm² at 100 °K from the value of the green luminescence decay time. The difference between their value and the larger estimate for σ_2 reported here seems to result from a longer experimental value for the magnitude of the green decay time, in conjunction with the use of $\tau_{1/e} \approx \tau_{2n} \equiv (1/\omega_2 - 1)^{-1} \tau_2$, which gives a lower bound on σ_2 . As discussed by J. S. Jayson *et al.* [J. Appl. Phys. **41**, 4972 (1970)] and in Ref. 8, a more general expression for the time decay of the green band is $1/\tau_{1/e} \cong 1/\tau_2 + (1 - s_2^j)/\tau_{2n}$, where the factor $1 - s_2^j$ represents the fraction of electrons thermalized from the S donors which are captured by other centers. (Thus, if $s_2^j = 1$, all thermalized electrons are recaptured by the S donors and the decay time is unperturbed by thermalization.) For the crystal studied

in Fig. 1, $s_2^j \approx 0.3$ at 60 °K. We might expect that the concentration of inadvertently present sulfur donors can vary widely from sample to sample, in some cases leading to s_2^j values close to unity, and hence to a greatly lengthened decay time for the green band.

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Threshold Energies for Electron-Hole Pair Production by Impact Ionization in Semiconductors*

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Threshold energies for energy- and momentum-conserving impact ionization of electron-hole pairs in actual semiconductors are determined by differential analysis of the energy-wave-vector relations of the participating charge carriers and phonons. A necessary condition for the initiating carrier to have minimum energy consistent with pair production is that the resultant carriers and all phonons involved have identical real-space velocities. This criterion allows calculations of ionization threshold energies for any semiconductor for which the one-electron-energy-wave-vector relationship is known. A step-by-step graphical procedure is presented for the calculation of threshold energies when the final particles are traveling along a principal axis of a semiconductor. Threshold energies resulting from the application of this procedure are presented for Si, Ge, GaAs, GaP, and InSb. Each of these materials exhibits numerous threshold energies for phononless ionization initiated by either type of carrier. The lowest thresholds for electron-initiated ionization without phonon assistance are 1.1, 0.8, 1.7, 2.6, and 0.2 eV relative to the conduction-band minima in Si, Ge, GaAs, GaP, and InSb, respectively. For ionization initiated by holes, the corresponding results are 1.8, 0.9, 1.4, 2.3, and 0.2 eV relative to the valence-band maximum.

I. INTRODUCTION

Carrier multiplication through impact ionization is an essential mechanism in the operation of many semiconductor devices. At present, however, the theoretical basis for understanding this effect is provided by a number of theories¹⁻⁴ of the statistical interrelation between the threshold energy for ionization, optical phonon energy, ionization mean free path, and the mean free path for optical phonon scattering. In these treatments, the value of the ionization threshold energy either is assumed or is used as an adjustable parameter to improve the fit of the theoretical curves to ionization coefficient data determined experimentally. For silicon, the

most widely studied material, a different threshold energy is required to fit the experimental data to each model. A possible explanation is the existence of a variation in the effective ionization threshold energy with electric field. Such an effect could result from the existence of multiple ionization thresholds. Thus it is clearly desirable to examine the validity of the concept of a single ionization threshold as characteristic of a particular material and to devise a means of determining threshold energies for realistic band structures.

A preliminary step in this direction has been made by Ahmad and Khokley.⁵ Using a two-valley model for silicon in the (100) direction, employing the density-of-states effective mass of electrons

near the conduction-band minima, and minimizing the energy associated with the final electrons only, they developed a graphical technique for the determination of a threshold energy for electron-initiated phononless impact ionization in silicon. Using this technique, they deduced threshold energies of 1.15, 1.52, and 2.06 eV relative to the conduction-band minimum. Prior to this, Hauser⁶ had employed an effective-mass approximation for both the valence and conduction bands to estimate the threshold energies for silicon, germanium, and gallium arsenide. Hauser neglected umklapp processes and did not use a consistent criterion to minimize the energy of the initiating particle. Thus his approach yielded threshold energies considerably higher than those deduced either in this paper or in that of Ahmad and Khokley. Additionally, Kane⁷ has pointed out the existence of an electron-initiated ionization process in silicon with a threshold energy of 1.1 eV relative to the conduction-band minimum.

In this paper we present a more general technique for determination of ionization threshold energies. Our method differs from that of Ahmad and Khokley in three ways: (i) It simultaneously minimizes the energy of the primary particle with respect to small changes of wave vector of *any* of the final particles and conserves total energy and total crystal momentum, (ii) it specifically includes the contribution of phonons, and (iii) it is applicable to any semiconductor for which the one-electron-energy-wave-vector relationship is known, and thus does not require further stylizing of the energy bands of the material. This is extremely important in cases where the effective-mass approximation is valid only for energies very near

the minima.

II. CRITERION OF EQUAL VELOCITIES: A NECESSARY CONDITION

Consider a typical ionization process. Subscripts for the appropriate variables are defined as follows (cf. Fig. 1): An initial electron in some conduction band i collides with the lattice and removes electron 1 from some valence band v . The resulting electrons 2 and 3 lie in the conduction bands c and c' , respectively. c and c' may be the same band. Phonons may be either emitted or absorbed. A similar diagram applies to ionization processes initiated by holes.

Following Fig. 1 and considering only carriers of the same type as the initiating carrier, the total energy E and total wave vector \vec{K} of the resultant carriers are expressible as follows:

$$E = E_c(\vec{k}_2) + E_{c'}(\vec{k}_3) - E_v(\vec{k}_1) + \sum_{\text{phonons } j} a_j \hbar \omega_\beta(\vec{k}_j) \quad (1)$$

and

$$\vec{K} = \vec{k}_2 + \vec{k}_3 - \vec{k}_1 + \sum_{\text{phonons } j} a_j \vec{k}_j, \quad (2)$$

where $E_\zeta(\vec{k})$ is the energy in band ζ of a charge carrier with wave vector \vec{k} , a_j may be any integer including zero (positive a_j correspond to phonon emission, negative a_j to phonon absorption), and $\omega_\beta(\vec{k}_j)$ is the angular frequency in branch β of a phonon with wave vector \vec{k}_j .

For a particular \vec{K} , minimization of the total energy of the final particles requires phonon absorption only ($a_j \leq 0$ for all j) and the following interrelations among the perturbations $d\vec{k}_1$, $d\vec{k}_2$,

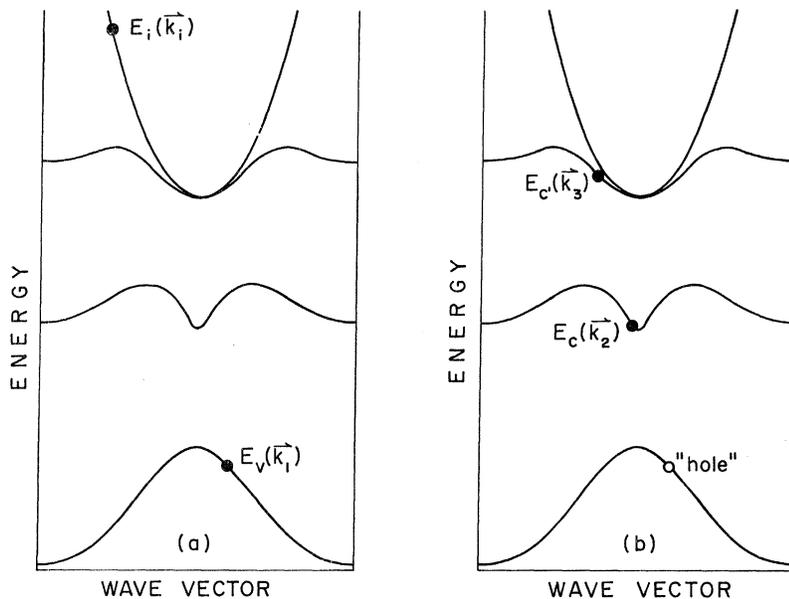


FIG. 1. Hypothetical impact-ionization process: (a) primary particles before ionization; (b) resultant particles immediately after ionization.

$d\vec{k}_3$, and $d\vec{k}_j$ of the wave vectors of the systems:

$$d\vec{k}_1 = d\vec{k}_2 + d\vec{k}_3 + \sum_{\text{phonons } j} a_j d\vec{k}_j \quad (3)$$

and

$$d\vec{k}_1 \cdot \vec{\nabla}_k E_v(\vec{k}_1) = d\vec{k}_2 \cdot \vec{\nabla}_k E_c(\vec{k}_2) + d\vec{k}_3 \cdot \vec{\nabla}_k E_c(\vec{k}_3) + \sum_{\text{phonons } j} a_j d\vec{k}_j \cdot \vec{\nabla}_k \hbar \omega_j(\vec{k}_j). \quad (4)$$

Utilizing the fundamental relation $\vec{v}_g = \hbar^{-1} \vec{\nabla}_k \mathcal{E}$, where \vec{v}_g , \vec{k} , and \mathcal{E} are the group velocity, wave vector, and energy, respectively, of a particle, Eq. (4) may be reexpressed as

$$0 = d\vec{k}_2 \cdot (\vec{v}_2 - \vec{v}_1) + d\vec{k}_3 \cdot (\vec{v}_3 - \vec{v}_1) + \sum_{\text{phonons } j} a_j d\vec{k}_j \cdot (\vec{v}_j - \vec{v}_1). \quad (5)$$

Since $d\vec{k}_2$, $d\vec{k}_3$, and the $d\vec{k}_j$ are linearly independent when \vec{k} is constant, Eq. (5) is satisfied if and only if $\vec{v}_1 = \vec{v}_2 = \vec{v}_3 = \vec{v}_j$ for all j . Thus a necessary condition for an initiating particle to have minimum energy consistent with pair production is that all the resultant "particles" have the same group velocity. If phonons are involved, this condition becomes extremely restrictive, since the resultant charge carriers must have the same velocity as the phonons. Since maximum phonon velocities are very small compared to maximum electron group velocities, only charge carriers located very near band extrema result from phonon-coupled threshold ionization processes.

III. CALCULATION OF IONIZATION THRESHOLDS

The criterion derived in Sec. II is not sufficient to guarantee the existence of ionization thresholds or the possibility of impact pair production in a particular material (cf. Fig. 2). Let $E_m(\vec{k}, n)$ be the minimum total energy (for two electrons, a hole, and a fixed number of phonons n) which satisfies Eq. (5). For this situation to describe an ionization event, conservation of energy and crystal momentum require that $E_m(\vec{k}, n)$ be equal to the energy in some energy band at wave vector \vec{k} —say, $E_i(\vec{k})$. There is no guarantee that this occurs at any particular \vec{k} .

Figure 2 illustrates a hypothetical set of curves of $E_m(\vec{k}, n)$ and $E_i(\vec{k})$ as functions of K for which a threshold does exist. $E_m(\vec{k}_1, n)$ is greater than $E_i(\vec{k}_1)$; hence an initiating carrier in band i with wave vector \vec{k}_1 has insufficient energy to cause an ionization. $E_m(\vec{k}_2, n)$ and $E_i(\vec{k}_2)$ are equal. Thus a threshold exists at \vec{k}_2 for an ionization process involving n phonons. Between \vec{k}_2 and \vec{k}_3 , $E_i(\vec{k})$ is greater than $E_m(\vec{k}, n)$ and an initiating carrier has more energy than required for the threshold process. In this range the cross section for ioniza-

tion may become finite, since the resultant carriers no longer need to have equal group velocities. Beyond \vec{k}_3 , $E_m(\vec{k}, n)$ again becomes greater than $E_i(\vec{k})$, thus making ionization impossible. The behavior of $E_m(\vec{k}, n)$ and $E_i(\vec{k})$ at \vec{k}_3 is distinct from their behavior at \vec{k}_2 and may be said to exhibit an "anti-threshold."

With the above in mind, it is clear that the determination of ionization thresholds by utilization of the criterion of equal velocities may be performed numerically if sufficiently precise band-structure data are available to allow meaningful differentiation of the energy-wave-vector relationship with respect to wave vector. The calculation of threshold energies may then be performed by a Newton's-method approach. If, at a particular value of \vec{k} , $E_i(\vec{k}) - E_m(\vec{k}, n) = \Delta E$, one should search for the threshold in the neighborhood of

$$\vec{k}' = \vec{k} + \frac{\Delta E \vec{\nabla}_k [E_i(\vec{k}) - E_m(\vec{k}, n)]}{|\vec{\nabla}_k [E_i(\vec{k}) - E_m(\vec{k}, n)]|^2}. \quad (6)$$

In a direct-gap semiconductor with spherical constant energy surfaces and constant effective masses m_c^* and $m_v^* = \gamma m_c^*$ for electrons in the conduction and valence bands, respectively, the threshold criterion requires that the relationship between the wave vectors of the final particles be

$$\vec{k}_v = \gamma \vec{k}_c, \quad (7)$$

where m_c^* and m_v^* are taken positive at the bottom of the conduction band and the top of the valence band, respectively. Thus, the energy and wave-vector relationships for a phononless threshold process initiated by an electron of energy $E_{th,e}$ are given by

$$\vec{k} = \vec{k}_c(2 + \gamma), \quad (8)$$

$$E_m(\vec{k}, 0) = \frac{\hbar^2 k_c^2}{2m_c^*} (2 + \gamma) + E_g = E_{th,e}, \quad (9)$$

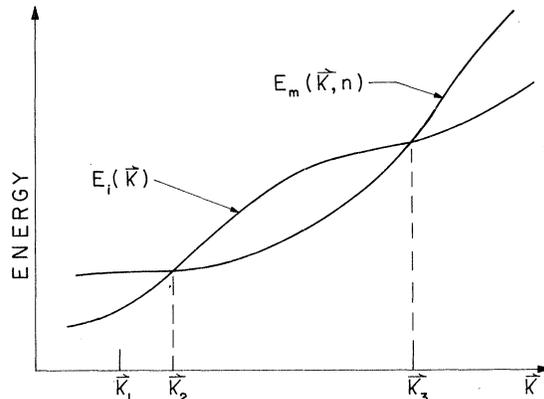


FIG. 2. Hypothetical set of curves of E_i and E_m as a function of K for a process which exhibits a threshold at \vec{k}_2 and an antithreshold at \vec{k}_3 .

TABLE I. Ionization threshold energies.

Material	Si	Ge	GaAs	GaP	InSb	
Band gap assumed (eV)	1.1	0.7	1.4	2.3	0.2	
Band structure	Indirect	Indirect	Direct	Indirect	Direct	
Direction	Initiation					
$\langle 100 \rangle$	electrons	1.1 U ^a	0.9 U, D	2.1 D*	2.6 U†	0.2(5) D
		1.5 D	1.0 D*, U	2.3 U*	3.0 D†	1.6 D
		1.6 U*	1.2 D	2.4 D*	3.1 D†	1.7 D*, D*
	holes	1.8 D	1.3 D, D*	1.7 D*	2.4 D ^b	0.2 D*
		2.1 D*	1.7 D*	1.9 D	...	0.6 D
		...	4.5 D*	2.5 D	...	2.2 D*
$\langle 111 \rangle$	electrons	3.1 U*	0.8 U, ^b U ^b	3.2 D†, D†	3.0 D†	0.2(5) D
		3.3 U*	2.5 D ^c	3.6 D†, D†	3.4 D†	...
		3.5 U*	2.6 D*	3.7 D†	3.5 U†, D† ^b	...
	holes	2.9 D*	0.9 D	1.6 D†	2.9 D†	0.4 D*
		4.4 D* ^c	1.0 D*	2.3 D†	3.6 D†	1.5 D*
		4.7 D*	1.4 D*	2.5 D†	...	1.8 D*
$\langle 110 \rangle$	electrons	2.1 U	1.1 D*	1.7 D	2.8 D†	0.2 D
		4.0 D*	1.2 D	1.9 D*	2.9 D†	1.6 D
		4.2 U*	1.3 U	2.2 D	3.3 D†	1.7 D*, D*
	holes	1.8 D	0.9 D*, D*	1.4 D*	2.3 D ^b	0.2 D*, D*
		4.0 D*	1.3 D	1.6 D*	2.6 D*	0.4 D
		4.1 D*	1.8 D*	1.9 D	2.8 D*	1.7 U* ^b , D*

^aD, direct process (no reciprocal-lattice translation vector involved); U, umklapp process; *, initiating carrier comes from other than the normal conduction or valence band; †, normal conduction or valence band cannot supply the initiating carrier (even if momentum conservation is neglected) because the energy range of the band is less than the band gap.

^bThe cross section for the process cited is likely to be very small, owing to the existence of an antithreshold within 0.1 eV of the threshold.

^cThis value obtained by a linear extrapolation of the light-hole band slightly beyond the limits of the graph.

and

$$E_c(\vec{K}) = \frac{\hbar^2 k_c^2}{2m^*} (2 + \gamma)^2 = E_{th,e}, \quad (10)$$

where E_g is the energy gap of the material. Upon eliminating k_c from Eqs. (9) and (10), the threshold energy for a phononless threshold process initiated by an electron is shown to be

$$E_{th,e} = E_g \left(\frac{2 + \gamma}{1 + \gamma} \right) \quad (11)$$

relative to the bottom of the conduction band. The corresponding threshold $E_{th,h}$ for ionization initiated by a hole is obtained by replacing γ by $1/\gamma$ in Eq. (11). Thus

$$E_{th,h} = E_g \left(\frac{1 + 2\gamma}{1 + \gamma} \right). \quad (12)$$

When γ is unity, both $E_{th,e}$ and $E_{th,h}$ are $\frac{3}{2}$ the band gap. Thus the well-known $\frac{3}{2}$ -band-gap rule¹ is a direct result of the application of the threshold criterion. It is interesting to note also that, irrespective of the value of γ , the sum of the electron and hole threshold energies is three times the band gap.

In many cases the available band-structure data are not sufficiently detailed to allow calculation of the threshold energies for processes involving resultant carriers lying off the principal axes of the reciprocal lattice or the investigator may not think that a complete characterization of all the thresholds available in a particular material is justified. In such cases a simple graphical technique may be employed. Using the technique, a complete set of thresholds for processes involving final particles traveling along the principal axes of the semiconductor can be computed in a few hours. Since the group velocity of charge carriers is proportional to the slope of the energy-vs-wave-vector curve, a trial set of final-particle wave vectors which satisfy the threshold criterion for one velocity along the chosen axis can be found by locating all the wave vectors at which each band being considered for the final particles has a chosen slope. A step-by-step procedure for finding a complete set of thresholds for electron-initiated ionization along the chosen axis using this principle is as follows.

(i) Find all the wave numbers $k_v(n)$, $k_c(m)$, and $k_{c'}(m')$ at which the bands v , c , and c' have a slope of zero.

TABLE II. Wave vectors of particles participating in threshold processes of Table I.

Material	Si	Ge	GaAs	GaP	InSb	
Direction	Initiation wave vectors					
⟨100⟩	electrons					
	k_i	-0.40	-0.42 ^a	0.60 ($\Gamma_{15}-X_3$)	-0.35 ($\Gamma_{15}-X_3$)	-0.05
	k_2, k_3	0.80, 0.80	0.79, 0.79	0.00, 0.70	0.85, 0.85	0.00, 0.00
	k_1	0.00	0.00	0.10	0.05	0.05
	holes					
	k_i	-0.46	-0.41 ^b	0.26 (lh) ^c	-0.95	0.04 (lh)
k_2, k_3	0.08, 0.08	0.10, 0.10	0.13, 0.13	0.01, 0.01	0.02, 0.02	
k_1	0.62	0.61	0.00	0.97	0.00	
⟨111⟩	electrons					
	k_i	-0.02 ($\Gamma_2'-L$) ^d	-0.24 ^e	0.15 ^f ($\Gamma_{15}-L$)	-0.10 ($\Gamma_{15}-L_3$)	-0.06
	k_2, k_3	0.99, 0.99	0.92, 0.92	0.73, -0.30	0.00, 0.00	0.00, 0.00
	k_1	0.00	0.08	0.28	0.10	0.06
	holes					
	k_i	-0.35 (lh)	-0.70	0.24 (lh)	0.40 (lh)	0.04 (lh)
k_2, k_3	0.15, 0.15	0.10, 0.10	0.12, 0.12	0.20, 0.20	0.02, 0.02	
k_1	0.65	0.90	0.00	0.00	0.00	
⟨110⟩	electrons					
	k_i	-0.47	0.92 ($\Gamma_{15}-K_1-X_1$)	-0.23	0.79 ($\Gamma_{15}-K_1-X_1$)	-0.03
	k_2, k_3	0.86, 0.86	0.00, 0.96	0.00, 0.00	0.00, 0.97	0.00, 0.00
	k_1	0.19	0.04	0.23	0.18	0.03
	holes					
	k_i	-0.57	0.18 ^g ($\Gamma_{25}'-K_1-X_4$)	0.14 ($\Gamma_{15}-K$)	-0.96	0.08 ^h ($\Gamma_{15}-K_1-X_3$)
k_2, k_3	0.16, 0.16	0.09, 0.09	0.07, 0.07	0.02, 0.02	0.04, 0.04	
k_1	0.89	0.00	0.00	1.00	0.00	

^aThese data are for the umklapp process. The corresponding data for the direct process are -0.10 ($\Gamma_2'-X_1$), 0.77, -0.87, 0.00.

^bThese data are for the D process. For the D* process the data are 0.18 (lh), 0.09, 0.09, 0.00.

^cWhere no ambiguity results, (lh) is used to denote the light-hole band.

^d L and K denote L and K points, respectively, beyond the range of the diagrams of Cohen and Bergstresser (Ref. 8).

^eFor the second process the data are -0.33, 0.89, 0.89, 0.11.

^fFor the second process the data are 0.13 ($\Gamma_{15}-L_3$), 0.73, -0.30, 0.30.

^gFor the second process the data are 0.12 ($\Gamma_{25}'-K$), 0.06, 0.06, 0.00.

^hFor the second process the data are 0.02 ($\Gamma_{15}-K$), 0.01, 0.01, 0.00.

(ii) Tabulate all possible sets of one $k_v(n)$, one $k_c(m)$, and one $k_{c'}(m')$.

(iii) For each combination find

$$K = k_c(m) + k_{c'}(m') - k_v(n) \quad (13)$$

and

$$E_m = E_c(k_c(m)) + E_{c'}(k_{c'}(m')) - E_v(k_v(n)). \quad (14)$$

If necessary, reduce K to a value within the first Brillouin zone.

(iv) For each band i being considered as a source of initiating particles, compare $E_i(K)$ with E_m .

(v) If $E_i(K) = E_m$, the combination of final particles being tested can result from an initial parti-

cle whose energy is a threshold energy or an anti-threshold energy.

(vi) Repeat steps (i)-(v) above for a set of slopes, increasing the slope until one of the bands v , c , or c' no longer has any segments exhibiting the slope chosen.

(vii) If $E_i(K) - E_m$ changes signs between steps (i) and (vi) above for two different slopes, a threshold or antithreshold has been bypassed. Either pick slopes intermediate between these two slopes until the threshold or antithreshold is found or interpolate between the two values of E_m or $E_i(K)$ to determine the threshold or antithreshold energy.

(viii) Separate thresholds from antithresholds

by evaluating the behavior of $E_i(K) - E_m$ for slopes above and below the slope at which $E_i(K) - E_m$ equals zero. If $E_i(K) - E_m$ becomes negative as $E_i(K)$ increases, the process discovered exhibits an anti-threshold at the point where $E_i(K) - E_m = 0$, since the energy of the final particles increases more rapidly than the energy of the initial particle. If $E_i(K) - E_m$ becomes positive as $E_i(K)$ increases, the process being examined exhibits a threshold at the point in question.

Processes involving phonons are completely exhausted at slopes very nearly equal to zero in the above procedure. Any difference between $E_i(K)$ and E_m must be compensated for by phonon emission or absorption.

We have applied the graphical technique to the evaluation of ionization threshold energies for carriers traveling along the $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ directions in Si, Ge, GaAs, GaP, and InSb using the band-structure diagrams of Cohen and Bergstresser.⁸ Where the band gaps of Cohen and Bergstresser differed from accepted values, the band gaps were corrected by arbitrarily shifting all conduction-band energies measured from the diagrams by the appropriate amount. In all cases, the final particles were assumed to lie in the lowest-lying conduction band or highest-lying valence band. All possible bands were investigated as sources of initiating carriers. Spin-orbit coupling effects were not included.

The results of this calculation are presented in Tables I and II. In Table I the three lowest threshold energies for each type of initiating carrier are given as a function of orientation. All energies are quoted in eV relative to the band edge. The estimated accuracy of these results is ± 0.2 eV. Table I also specifies whether the processes are direct or umklapp processes and if the initiating carrier comes from other than the normal conduction or valence band. When two processes have the same threshold, this too is indicated.

Table II specifies the wave vectors of the particles which participate in the process with the lowest threshold energy listed in each box in Table I.

Wave vectors in the $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ directions are quoted as fractions of the lengths of $(1, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and $(1, 1, 0)$, respectively. The notation for the various wave vectors is consistent with Fig. 1. The estimated accuracy of these results is ± 0.05 times the appropriate length. If the initiating carrier comes from other than the normal conduction or valence band, the band which supplies the initiating carrier is entered in Table II. To facilitate the use of this table in conjunction with the diagrams of Cohen and Bergstresser, the bands are described in terms of the high-symmetry points which they connect.

IV. CONCLUSIONS

From Table I the following conclusions and observations may be drawn.

(i) Every material studied has a multiplicity of thresholds even without considering phonon-coupled processes. Thus the existence of electric-field-dependent effective threshold energies is extremely likely. The threshold actually measured will be a function of the sensitivity of the measurement technique, the electric field, the lattice temperature, and the relative magnitudes of the cross sections of the processes associated with the various thresholds.

(ii) In no material is the lowest threshold for electron-initiated ionization greater than $\frac{3}{2}$ the band gap.

(iii) Only in silicon is the lowest threshold energy for hole-initiated ionization greater than $\frac{3}{2}$ the band gap.

(iv) No direct-gap material has a lowest threshold involving an umklapp process, whereas the lowest threshold energies in indirect-gap materials are umklapp processes for electron initiation and direct processes for hole initiation.

(v) Electron-initiated ionization in GaP is determined by the structure of high-lying conduction bands, and therefore the thresholds quoted for electron-initiated ionization in this material are probably the least accurate in these tables.

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