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First-order optical and intervalley scattering in semiconductors

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The scattering rate and momentum relaxation time for nonpolar optical and intervalley scattering is determined for the case in which the interaction matrix element is of first order in the wave vector of the phonon. This process is expected to be important in many cases in which the zero-order interaction is forbidden by symmetry selection rules. The results are applied to silicon where, for reasonable values of the coupling constants, scattering via first-order coupling is comparable to the weakly coupled value that until now has been improperly assumed for the zero-order low-energy phonon interaction, which is actually forbidden.

I. INTRODUCTION

The scattering of electrons by zone-center optical and intervalley phonons in semiconductor crystals has been treated rather extensively by many authors. In particular, the polar optical-phonon interaction was treated by Fröhlich,[1] Callen,[2] and Ehrenreich.[3] Consideration of the nonpolar optical interaction with electrons was carried out by Seitz[4] and Harrison.[5] The nonpolar optical interaction is important for intravalley scattering as well as being utilized for scattering of electrons (or holes) between different minima of the conduction (or valence) band. This latter interaction is important for scattering of carriers in semiconductors with many-valley band structure, and also in the Gunn effect,[6] where scattering occurs between different sets of equivalent minima. Harrison[5] pointed out that the nonpolar optical matrix element may be either of zero or higher order in the wave vector of the phonon. In subsequent treatments of electron transport in which the nonpolar interaction is important, only the zero-order term has been considered, generally owing to the impression that the higher-order terms are much smaller. Although this is usually the case, there arise many cases in which the zero-order term is forbidden by the symmetry of the states involved.[5,7-9] In these cases, the first-order term becomes the leading term, and can become significant in many instances.

In the present paper, the scattering rate and momentum relaxation time are calculated for the first-order nonpolar optical and intervalley matrix element in semiconductors. By way of example, the results are applied to silicon and provide a resolution of a dilemma that has been associated with electron transport in silicon for some time.

Long[10] developed a model of transport in silicon in which electron scattering occurring between the six equivalent minima of the conduction band dominated the mobility. In doing so, he used two effective phonons, with activation temperatures of 630 and 190 K, to represent the various phonons involved in the scattering. In his treatment, he found that the low-energy phonon (190 K) was weakly coupled with respect to the higher-energy phonon. It was subsequently found, however, that the symmetry properties of silicon are such that all of the transitions which could occur via phonons which would contribute to the effective low-energy phonon are forbidden transitions.[11,12] Yet most conduction studies, even now, imply the presence of interactions via these phonons, and calculations still include *ad hoc* interactions due to these phonons.[13] In particular, magnetophonon resonance studies explicitly demonstrate the occurrence of scattering via these phonons,[14] in about the strength determined by Long. As a result of the present calculation, it is found that for reasonable values of the coupling constants, scattering via first-order interactions is comparable to the weak zero-order interaction improperly utilized by Long for the 190-K phonon. Long's results were fortuitous in the sense that over the temperature range where this phonon is expected to make a sizeable contribution to the mobility, the forced inclusion of weak zero-order processes roughly accounted for the proper first-order interaction.

II. FIRST-ORDER SCATTERING

In scattering by nonpolar optical and intervalley phonons, Seitz[4] pointed out that the part of the matrix element arising from an integration over the electron coordinates could be written as $D_t K$, where D_t is an interaction constant, or deformation potential, having the units of energy, and K is a vector of the reciprocal lattice. Harrison[5] and Meyer[15] modified this to the form $\vec{D}\cdot\vec{d}$, where $\vec{D}$ is now the energy shift per unit displacement and $\vec{d}$ is the relative displacement of the sublattices. If the zero-order matrix element for the interaction is forbidden by symmetry, then it is expected that $\vec{D}$ and D_t are identically equal to zero. In first-order processes, this interaction gives rise to a term of the form $D_1\vec{q}\cdot\vec{d}$, where D_1 is the energy shift, or first-order deformation potential, and $\vec{q}$ is the wave vector of the phonon.[16] As a result, the absolute square of the first-order, nonpolar optical matrix element can be written

$$|\langle \vec{k}\pm\vec{q}|H'|\vec{k}\rangle|^2=\frac{D_1^2\hbar q^2}{2V\rho_m\omega_0}\,(N+\tfrac{1}{2}\pm\tfrac{1}{2}), \tag{1}$$

where $\vec{k}$ is the electron wave vector, V is the volume of the crystal, ρ_m is the mass density, ω_0 is the phonon radian frequency, and N is the phonon occupation factor, represented by the Bose-Einstein distribution. The upper sign is for the emission of phonons and the lower sign is for the absorption of phonons by the electrons.

To obtain the total transition rates, a sum over the various phonon wave vectors must be carried out. Then, the reciprocal scattering time, or scattering rate, is given by

$$\Gamma=\frac{1}{\tau}=\frac{2\pi}{\hbar}\sum_{\vec{q}}|\langle \vec{k}\pm\vec{q}|H'|\vec{k}\rangle|^2\delta(E'-E\pm\hbar\omega_0), \tag{2}$$

where E is the carrier energy. Using Eq. (1) this becomes

$$\Gamma=\frac{\pi D_1^2}{V\rho_m\omega_0}\,(N+\tfrac{1}{2}\pm\tfrac{1}{2})\sum_{\vec{q}}q^2\,\delta(E'-E\pm\hbar\omega_0). \tag{3}$$

Actually, N has a very weak dependence on q through the dispersion of the optical phonon. However, in practice this dispersion is so weak that this dependence can be neglected. The sum over $\vec{q}$ can be taken into an integral, with $\vec{k}$ taken as the polar angle, via

$$\sum_{\vec{q}}\rightarrow\frac{V}{8\pi^3}\int\int\int q^2(\sin\theta)\,d\theta\,d\phi\,dq. \tag{4}$$

The integral over ϕ is readily carried out, and

$$\Gamma=\frac{D_1^2}{4\pi\rho_m\omega_0}\bigg(N\int\int q^4(\sin\theta)\,\delta(E'-E-\hbar\omega_0)\,d\theta\,dq + (N+1)\int\int q^4(\sin\theta)\times\delta(E'-E+\hbar\omega_0)\,d\theta\,dq\bigg). \tag{5}$$

The integral over θ involves the argument of the δ function, since this argument can be written

$$E'-E\pm\hbar\omega_0=\pm(\hbar^2kq/m)\cos\theta+\hbar^2q^2/2m\pm\hbar\omega_0, \tag{6}$$

where m is the effective mass of the carriers. The integration over this function in turn sets the limits on the integration over q. Thus,

$$\Gamma=\frac{mD_1^2}{4\pi\hbar^2\rho_m\omega_0k}\left(N\int_{L-}^{U-}q^3\,dq+(N+1)\int_{L+}^{U+}q^3\,dq\right), \tag{7}$$

where the limits are

$$L-=k[(1+\hbar\omega_0/E)^{1/2}-1], \tag{8a}$$

$$U-=k[(1+\hbar\omega_0/E)^{1/2}+1], \tag{8b}$$

$$L+=k[1-(1-\hbar\omega_0/E)^{1/2}], \tag{8c}$$

$$U+=k[1+(1-\hbar\omega_0/E)^{1/2}]. \tag{8d}$$

The integration over q is straightforward and

$$\Gamma=\frac{mD_1^2k^3}{2\pi\rho_m\hbar^2\omega_0}\left[N\left(1+\frac{\hbar\omega_0}{E}\right)^{1/2}\left(2+\frac{\hbar\omega_0}{E}\right)+(N+1)\left(1-\frac{\hbar\omega_0}{E}\right)^{1/2}\left(2-\frac{\hbar\omega_0}{E}\right)\times u_0(E-\hbar\omega_0)\right], \tag{9}$$

where u_0 is the unit step function, defined by

$$u_0(x)=\begin{cases}0, & x<0,\\ 1, & x\geqslant 0.\end{cases} \tag{10}$$

Equation (9) can be rewritten in terms of the energy only, and

$$\Gamma=\frac{(2m)^{1/2}m^2D_1^2}{\pi\rho_m\omega_0\hbar^5}\Big[N(E+\hbar\omega_0)^{1/2}(2E+\hbar\omega_0)+(N+1)(E-\hbar\omega_0)^{1/2}\times(2E-\hbar\omega_0)^{1/2}\,u_0(E-\hbar\omega_0)\Big]. \tag{11}$$

This result differs from the zero-order result only through the additional energy terms $(2E\pm\hbar\omega_0)$ and the appropriate constants to make the term dimensionless. These introduce just the factor

$$[(2k\pm q)/K]^2(D_1/D_t)^2 \tag{12}$$

as might be expected.

In order to calculate the momentum relaxation time, the result in Eq. (11) must be averaged over the distribution function. Rather than just computing $\langle\tau\rangle$, for a true momentum relaxation time the rate of loss of crystal momentum by the carriers to the lattice must be calculated.[17] This involves just the scattering rate Γ calculated above. For the distribution function, a drifted Maxwellian is utilized. Of course, the symmetrical part of the distribution function f_0 makes no contribution to the momentum average, and the leading term involves the f_1 portion of the distribution function. Then

$$\frac{1}{\tau_m}=\frac{(2m)^{1/2}m^2D_1^2}{\pi\rho\omega_0\hbar^5}\left[N\langle(E+\hbar\omega_0)^{1/2}(2E+h\omega_0)\rangle+(N+1)\langle(E-h\omega_0)^{1/2}(2E-\hbar\omega_0)u_0(E-\hbar\omega_0)\rangle\right]\ , \tag{13}$$

where the averages follow from the f_1 term as

$$\langle g(E)\rangle=\left(\int_0^\infty E^{3/2}g(E)e^{-E/k_BT}dE\right)\Big/\left(\int_0^\infty E^{3/2}e^{-E/k_BT}dE\right). \tag{14}$$

The integrals are somewhat tedious, but routine. The result is

$$\frac{1}{\tau_m}=\frac{(2mk_BT)^{1/2}m^2D_1^2}{\pi^{3/2}\rho_m\hbar^4}NF(x), \tag{15}$$

where $x=\hbar\omega_0/k_BT$, and

$$F(x)=xe^{x/2}[4K_2(\tfrac{1}{2}x)+\tfrac{1}{3}xK_1(\tfrac{1}{2}x)], \tag{16}$$

where K_1 and K_2 are modified Bessel functions of the second kind. A similar procedure can be carried out for the equivalent zero-order process, and the ratio of the two is

$$\frac{\tau_{m0}}{\tau_{m1}}=\frac{2m\omega_0}{\hbar}\left(\frac{D_1}{D}\right)^2\left(x+12\frac{K_2(\frac{1}{2}x)}{K_1(\frac{1}{2}x)}\right). \tag{17}$$

In addition to the dependence upon the phonon energy and coupling constants, the relative strengths of the two orders are temperature dependent through the modified Bessel functions.

III. APPLICATION TO SILICON

The conduction band of silicon is characterized by six equivalent minima located along Δ approximately 83% of the way to X from the Γ point. Intervalley scattering can proceed by two different groups of phonons. One set, denoted g phonons, couples one valley to its partner along the [100] axis. The other set, denoted f phonons, couples this valley to the four valleys lying on the [010] and [001] axes. Because the valleys lie more than half way to X, all of these processes involve umklapp processes. The net g-phonon wave vector corresponds to $0.34X$, while the f phonons arise from phonons whose wave vector lies along Σ extended along S in the plane perpendicular to the [100] axis. These latter phonons possess Σ symmetry, but they lie very near the X point so that their energies are very near to those of the X point.[7,10] Because of the multitude of phonons possible, Long[10] used just two equivalent phonons to treat transport in silicon over the temperature range 30–350 K. One of these was high-energy 630-K phonon used to represent the effect of the LO + TO intervalley processes and the LO intravalley process. The other was a 190-K phonon used to represent the effect of the LA + TA interactions. Not considering the possibility that many of these processes were forbidden, he determined values for the coupling constants by fitting the experimental data for various transport measurements. In doing so, he found that the low-energy process was considerably weaker than the high-energy process, with the two contributing in the ratio 0.15/2. Subsequently, Streitwolf[11] and Lax and Birman,[12] in considering the crystal symmetry of silicon, pointed out that only the Δ_2' (LO) phonon was allowed for the g-phonon interaction, and the Σ_1 (LA, TO) was allowed for the f-phonon interaction. Both of these processes would contribute to Long's 630-K phonon. All of the processes which could contribute to the low-energy 190-K phonon are, in fact, forbidden by symmetry. Norton *et al.*,[13] after noting the constraints introduced by symmetry, recalculated the transport properties, but they still were required to include *ad hoc* the low-energy phonon in order to fit the experimental data. The most explicit evidence for the presence of the phonons is found in the magnetophonon resonance data of Portal *et al.*[14] Magnetophonon resonance occurs when the Landau-level separation is a submultiple of the phonon energy, or $\hbar\omega_0=n\hbar\omega_c$, where n is an integer and $\omega_c=eB/m$ is the cyclotron resonance frequency. In the measurements of magnetophonon resonance in silicon, oscillatory series were observed which correspond to most of the phonons mentioned at the start of this section, and the relative strengths of the various phonons were estimated to be near that assumed by Long. Although the low-energy phonons are explicitly forbidden in the zero-order interaction, their observation in experimental measurements suggests that they are interacting via a first-order interaction. The occurrence of this interaction via a first-order process would also explain why the low-energy process is found to be so weakly coupled.

To investigate the role of first-order optical and intervalley phonon interactions, the mobility of silicon is calculated utilizing acoustic intravalley scattering and intervalley scattering by two equivalent phonons. A 630-K high-energy phonon is included via a zero-order process, and a low-energy 190-K phonon is included via the above-calculated first-order process. The mass involved is the density-of-states effective mass,[16,18] $m=(m_l m_t^2)^{1/3} = 0.57 m_0$. Murase *et al.*[19] determined values for the two deformation-potential constants Ξ_d (dilatation) and Ξ_u (shear) for the acoustic interaction. The values found were -6.0 and 9.0 eV, respectively. Krowne and Holm-Kennedy[20] used these values to estimate the values of the intervalley coupling constants appropriate to Long's calculations from the above values for the deformation potentials. These yielded a value for the zero-order coupling constant of 7.6×10^8 eV/cm, after correction for the number of equivalent values, for the high-energy phonon. If this value of D is used to get a value for Seitz's[4] optical deformation potential, D_t, a value of 13 eV is found. The nearness of this number to the acoustic deformation potentials suggests that a value for D_1 near the acoustic value is appropriate, especially since this latter process is also a first-order interaction. The effective acoustic deformation potential obtained from Murase *et al.*[19] is about 3.0 eV. A good fit to the experimental mobility data is obtained by using a value of 3.0 eV for the acoustic deformation potential, 9.0×10^8 eV/cm for the zero-order high-energy phonon, and 5.6 eV for the low-energy first-order phonon interaction. This is shown in Fig. 1. In Fig. 2, the relative contributions to the mobility of the three phonon processes is illustrated over the same temperature range.

As a further consideration, the relative strength of the first-order interaction to the *ad hoc* zero-order interaction introduced by Long can be determined by using Eq. (17) above. The assumed value utilized by Long in the low-energy zero-order process was shown by Krowne and Holm-Kennedy[20] to give a deformation coupling constant of 2.4×10^8 eV/cm. Using this value and the 14.3-eV value for D_1, the coefficient of the third term on the right-hand side of Eq. (17) is 1.33×10^{-2}. For

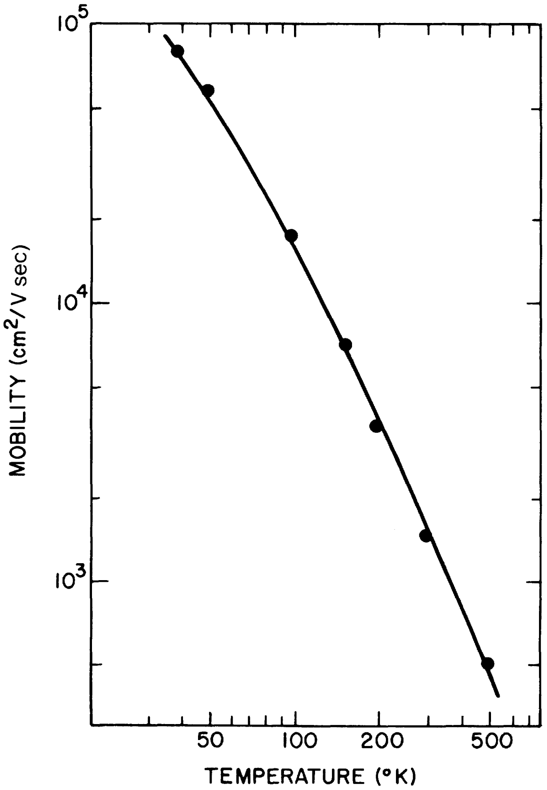

FIG. 1. Mobility as calculated for acoustic intravalley scattering and intervalley scattering via a high-energy (630-K) zero-order phonon and a low-energy (190-K) first-order coupled phonon. Solid curve is the experimental data taken from Refs. 10 and 13, and the circles arise from the present calculation.

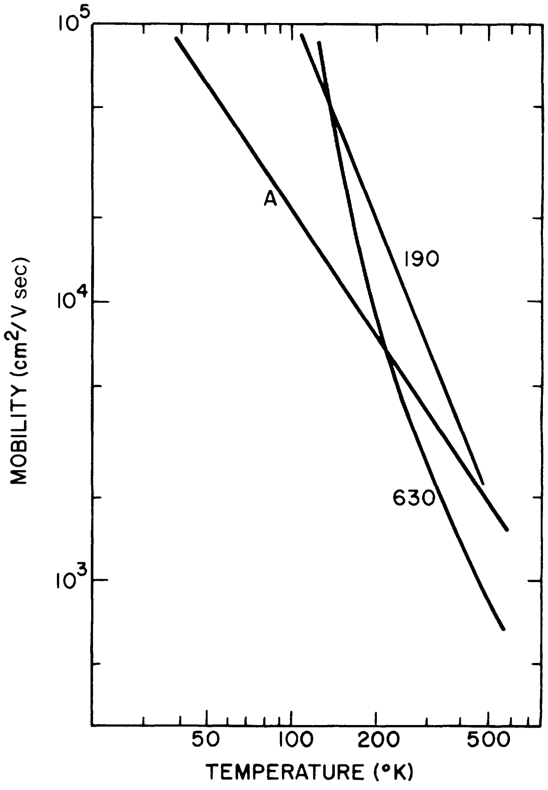

FIG. 2. Relative contributions to the mobility from the three phonon processes. Curves labeled 630 and 190 represent the mobility of the high-energy zero-order coupled phonon and the low-energy first-order coupled phonon, respectively. Curve labeled A is the acoustic-phonon contribution.

the 190-K phonon, the third term is a slowly varying function of temperature, varying from 16.4 at 100 K to 125 at 500 K. As a result, the right-hand side of Eq. (17) takes on values of 0.22, 0.62, 0.77 and 1.07 at temperatures of 100, 150, 200, and 300 K, respectively. Thus, in this range of temperature, and for these values of the coupling constants, the improperly assumed zero-order interaction gives a contribution to the mobility that effectively approximates the true first-order interaction, although a slightly stronger-coupled high-energy phonon must be used to fit the mobility.

IV. CONCLUSIONS

The first-order optical and intervalley scattering rate and momentum relaxation time have been calculated. This process is expected to be important in many cases where the zero-order interaction is forbidden by symmetry selection rules. This is the case for many of the semiconductors such as silicon and germanium. Other semiconductors exist such as the lead salts in which all intervalley scattering processes are forbidden to zero order. It may well be expected that the first-order interaction will be important in these materials, especially to equilibriate the electron population in the various valleys of the multivalley band structure.

In the case of silicon, consideration of the ratio of first-order to zero-order processes, in which the latter was included by Long,[10] shows that for reasonable values of the coupling constants, calculations of the mobility contribution of these two processes yield comparable results in some temperature ranges. The low-energy 190-K phonon can be expected to have its major contribution below 200 K. At higher temperatures, the high-energy phonon will dominate the mobility. In this low-temperature range, the right-hand side of Eq. (17) takes on values near to unity. As a result, although the zero-order process is explicitly forbidden and the coupling constant should be zero, the *ad hoc* inclusion of this process with a coupling constant as used by Long[10] and by Norton *et al.*[13] does in fact give a fair approximation to the actual inclusion of this first-order interaction. This result is fortuitous, though since the detailed temperature variations are different for the two orders. This effect is masked by the strong high-energy interaction in this case, a result that will not in general occur in other semiconductors.

The choice of silicon in which to illustrate this first-order interaction is not the best choice owing to the much higher scattering rates that arise from the high-energy phonons. However, it is important due to the large amount of work on high-electric-field transport that is still going on. The proper inclusion of the low-energy phonon in the transport process via a first-order interaction will greatly affect the results of such work. The role of this interaction in other semiconductors as well as in inversion layers in silicon will be treated elsewhere.

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[1] H. Fröhlich, Proc. R. Soc. A 160, 230 (1937).

[2] H. Callen, Phys. Rev. 76, 1394 (1949).

[3] H. Ehrenreich, J. Phys. Chem. Solids 2, 131 (1957).

[4] F. Seitz, Phys. Rev. 73, 549 (1948).

[5] W. A. Harrison, Phys. Rev. 104, 1281 (1956).

[6] See, e.g., E. M. Conwell, *High Field Transport in Semiconductors* (Academic, New York, 1967).

[7] M. Lax and J. J. Hopfield, Phys. Rev. 124, 115 (1961).

[8] J. L. Birman, Phys. Rev. 127, 1093 (1962).

[9] J. L. Birman, M. Lax, and R. Loudon, Phys. Rev. 145, 620 (1966).

[10] D. Long, Phys. Rev. 120, 2024 (1960).

[11] H. W. Streitwolf, Phys. Status Solidi 37, K47 (1970).

[12] M. Lax and J. L. Birman, Phys. Status Solidi B 49, K153 (1972).

[13] For a thorough discussion of this state of affairs, as well as a recalculation of the various transport processes, see P. Norton, T. Braggins, and H. Levinstein, Phys. Rev. B 8, 5632 (1973).

[14] J. C. Portal, L. Eaves, S. Askenazy, and R. A. Stradling, in *Proceedings of the International Conference on the Physics of Semiconductors, Stuttgart,* edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974), p. 259.

[15] H. J. G. Meyer, Phys. Rev. 112, 298 (1958).

[16] Actually, D_1 should be a second-rank tensor with the full symmetry of the group of the electron wave vectors, just as is the case for the acoustic deformation potential, in which there are dilatation and shear components. The value used here is an effective deformation potential in the same sense as an effective value is obtained for the acoustic deformation potential by C. Herring [Bell. Syst. Tech. J. 34, 237 (1955)], and is an actual value only for spherical constant-energy surfaces. This form is due to Harrison, Ref. 5.

[17] The details of this are straightforward and have been utilized, for example, to determine the momentum relaxation time for the zero-order process. A discussion of the method can be found in Ref. 6 or in E. G. S. Paige [*Electrical Conductivity of Germanium* (Academic, New York, 1964)].

[18] J. M. Ziman, *Electrons and Phonons* (Oxford U.P., London, 1960).

[19] K. Murase, K. Enjouji, and E. Otsuka, J. Phys. Soc. Jpn. 29, 1248 (1970).

[20] C. M. Krowne and J. W. Holm-Kennedy, Surf. Sci. 46, 197 (1974).