[6] In Refs. 2 and 3, we discuss this mapping of the zincblende Brillouin zone into the chalcopyrite Brillouin zone and give references to the theoretical work in the Russian literature.

[7] J. L. Shay and E. Buehler, Phys. Rev. Letters 26, 506 (1971).

[8] N. A. Goryunova, L. B. Zlatkin, and E. K. Ivanov, J. Phys. Chem. Solids 31, 2557 (1970). These authors also ignore the distinction between birefringence ($B \equiv n_e - n_0$) and the effective birefringence [$B - \lambda(dB/d\lambda)$] determined from interference measurements. This can lead to serious errors when discussing phase matching of nonlinear interactions.

[9] N. A. Goryunova, I. I. Tychina, and R. Yu. Khansevarov, Sov. Phys. Semicond. 1, 110 (1967).

[10] N. A. Goryunova, S. M. Ryvkin, G. P. Shpenikov, I. I. Tychina, and V. G. Fedotov, Phys. Status Solidi 28, 489 (1968).

[11] A. P. Serednii, N. A. Goryunova, I. I. Tychina, G. F. Nikolskaya, I. V. Evfimovskii, A. N. Novikova, and I. S. Kovaleva, Phys. Status Solidi 34, 439 (1969).

[12] V. G. Fedotov, E. I. Leonov, V. N. Ivakhno, N. A. Goryunova, and I. I. Tychina, Sov. Phys. Semicond. 3, 1470 (1970).

[13] V. Rehn and D. Kyser, Phys. Rev. Letters 18, 848 (1967).

[14] J. J. Hopfield, J. Phys. Chem. Solids 15, 97 (1960). Our sign convention for Eqs. (1) and (3) is in agreement with this reference.

[15] Our symmetry notation is taken from G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, Mass., 1963).

[16] A. S. Borshchevskii, N. A. Goryunova, F. T. Kesamanly, and D. N. Nasledov, Phys. Status Solidi 21, 9 (1967).

[17] F. H. Pollak and M. Cardona, Phys. Rev. 172, 816 (1968).

[18] We have taken experimental values for deformational potentials from the summary by P. Lawaetz, Phys. Rev. (to be published).

[19] N. A. Goryunova, A. S. Poplavnoi, Yu. I. Polygalov, and V. A. Chaldyshev, Phys. Status Solidi 39, 9 (1970).

[20] E. J. Johnson, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1967), Vol. 3, p. 153.

[21] R. A. Forman, D. E. Aspnes, and M. Cardona, J. Phys. Chem Solids 31, 227 (1970), and references cited therein.

[22] M. D. Sturge, Phys. Rev. 127, 768 (1962).

[23] J. L. Shay, Phys. Rev. B 2, 803 (1970).

[24] T. S. Moss and T. D. F. Hawkins, Infrared Phys. 1, 111 (1961).

[25] D. D. Sell and P. Lawaetz, Phys. Rev. Letters 26, 311 (1971).

[26] C. W. Higginbotham, M. Cardona, and F. H. Pollak, Phys. Rev. 184, 821 (1969); P. Y. Yu, M. Cardona, and F. H. Pollak, Phys. Rev. B 3, 340 (1971).

[27] G. D. Boyd, E. Buehler, and F. Storz, Appl. Phys. Letters 18, 301 (1971).

[28] R. M. Martin (unpublished).

PHYSICAL REVIEW B VOLUME 4, NUMBER 8 15 OCTOBER 1971

Polar Mobility of Holes in III-V Compounds

J. D. Wiley
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 10 May 1971)

Ehrenreich has shown that the transition probability for scattering from state $\vec{k}$ to state $\vec{k}'$ depends on the overlap between initial- and final-state wave functions $G(\vec{k}, \vec{k}')$. This function has been calculated for intraband and interband scattering in the p-type III-V compounds using Kane's valence-band wave functions. A simple model is proposed for polar-mode scattering in the valence bands and it is shown that the polar mobility is nearly four times larger than previously calculated for p-type III-V compounds. Approximately half of this increase is a consequence of the reduced overlap of p-like wave functions, and the other half is contributed by the presence of high-mobility carriers in the light-hole band. It is shown that the p-GaP Hall mobility data of Casey, Ermanis, and Wolfstirn can be fitted quite well throughout the lattice scattering regime and that the dominant scattering mechanisms are acoustic and nonpolar optical modes.

I. INTRODUCTION

It is well known[1-3] that the magnitude of the room-temperature Hall mobility in lightly doped, p-type III-V semiconductors is in good agreement with the values calculated using Ehrenreich's[4,5] expression for polar mobility[6] μ_{PO}. The temperature dependence of μ_{PO} is in disagreement with experiment above room temperature but this can be somewhat improved by allowing the effective mass or dielectric constants to vary with temperature. In reporting the agreement in magnitudes, it is usually pointed out that the expression for the polar mobility contains no adjustable parameters (all the parameters being independently determined in other experiments). Thus, it is concluded, polar-mode scattering must be dominant in p-type as well as n-type III-V compounds.

The fact that μ_{PO} agrees so well with experimental room-temperature hole mobilities should be somewhat surprising for two important reasons. (i) The expression[6] for μ_{PO} was derived assuming a single band of carriers with s-like wave functions. Any theory of polar scattering in the valence bands must take account of the predominantly p-like symmetry of the wave functions and the simultaneous presence of two types of charge carriers (light and heavy holes). (ii) If polar-mode scattering completely explains the magnitude of the mobility at 300 °K then it is necessary to explain why acoustic- and nonpolar-optical- (NPO) mode scattering are so much weaker in p-type III-V compounds than they are in p-Ge and p-Si where they are the *only* lattice scattering mechanisms. This is usually done by assuming unrealistically low values for the deformation potentials. For example, the acoustic-mode deformation potential is often taken to be $E_{AC} \approx 1$ eV. In contrast, experimental values of E_{AC} for Ge and Si are in the range 3–8 eV.[7–9] There is no reason to believe that E_{AC} should be so much smaller in compound semiconductors.

The question of the relative importance of acoustic-, NPO-, and polar-mode scattering in p-type III-V compounds was discussed in an earlier paper[7] (hereafter referred to as I) in which it was concluded that it is possible to fit the magnitude and temperature dependence of the Hall mobilities in p-type Ge, Si, GaP, GaAs, InP, and AlSb without including any polar-mode scattering. The theoretical expression for μ included acoustic and NPO scattering and treated two-band transport in an approximate way.[7,10] The deformation potentials used in fitting the data have since been shown to be reasonable on theoretical grounds.[8] It was further shown in I that, while polar-mode scattering may not be entirely absent in p-type materials, it must clearly be weaker than the predictions of the standard theory.[5,11]

The purpose of the present paper is to reconsider polar-mode scattering for p-type materials using the correct wave functions and taking approximate account of the effect of the light-hole band. It will be shown that polar-mode scattering in the valence bands is indeed weaker than previously thought. The p-like symmetry of the wave functions and the presence of high-mobility light holes each leads to a reduction of the scattering probability by a factor of about 2. The over-all polar mobility is thus about 3.5 to 4 times higher than previously calculated.

In Sec. II, the problem of scattering in the valence bands is shown to hinge upon the evaluation of Ehrenreich's function[4,12] $G(\vec{k}, \vec{k}')$ which represents the overlap between initial- and final-state wave functions. In Sec. III, $G(\vec{k}, \vec{k}')$ is evaluated for intraband and interband scattering using Kane's[13] wave functions. Section IV contains a discussion of the effects of $G(\vec{k}, \vec{k}')$ on the mobility. A simple expression is derived for the polar mobility in p-type III-V compounds. Section V is a summary of the results and conclusions of this work.

II. SCATTERING IN VALENCE BANDS

Ehrenreich[4] has shown that the matrix element for scattering from state $\vec{k}$ to state $\vec{k}'$ includes a multiplicative factor given by

$$G(\vec{k}, \vec{k}') = \tfrac{1}{2} \sum_{\mu_1, \mu_2} \left| \int U^{*}_{\mu_2 \vec{k}'}(\vec{r}) U_{\mu_1 \vec{k}}(\vec{r})\, d\vec{r} \right|^2, \quad (1)$$

where the sum is over spin states and the functions $U(\vec{r})$ are the cell-periodic parts of the Bloch functions. Physically, G represents the overlap between the initial- and final-state wave functions. For isotropic (s-like) wave functions the overlap is unity for all $\vec{k}$ and $\vec{k}'$. When there is an admixture of anisotropic wave functions the overlap is, in general, less than unity for all scattering angles except $\gamma = 0$. Ehrenreich[4] showed that for electrons in InSb the admixture of valence-band (p-like) wave functions for $k > 0$ results in a decrease in the scattering and a consequent increase in the mobility. This effect is usually ignored for low-field transport in s-like conduction bands but must be taken into account for high-field transport[14–16] and for transport in the predominantly p-like valence bands.

There have been several detailed theoretical treatments of acoustic and NPO scattering in Ge-like valence bands[17–21] in which proper account was taken of the overlap integral $G(\vec{k}, \vec{k}')$. Unfortunately, these calculations are not easily repeated for the routine analysis of experimental data and hence have found little application. The method which is most commonly used to describe acoustic and NPO scattering in the valence bands is that of Brown and Bray.[10] This method was slightly reformulated in I and applied to the III-V compounds in a way which automatically incorporates the effects of $G(\vec{k}, \vec{k}')$. This point will be discussed in Sec. IV B.

In the case of polar-mode scattering, the expression normally used for μ_{PO} is[5]

$$\mu_{PO}\,(\mathrm{cm^2/V\,sec}) = 0.199 (T/300)^{1/2} (e/e^*)^2 (m_0/m^*)^{3/2} \times (10^{22} M)(10^{23} v_a)(10^{-13} \omega_0)(e^{z} - 1)[e^{-z} G(1)]\,, \quad (2)$$

where T is the absolute temperature, e^* is the Callen effective charge, m^* is the effective mass, M is the reduced mass of a unit cell in g, v_a is the volume of the unit cell in cm^3, ω_0 is the angular frequency of LO phonons, $z = \hbar\omega_0 / k_B T$, and the function $e^{-z} G(1)$ is given graphically in Fig. 2 of Ref. 5. As was noted in Sec. I, this expression was derived for a single s-like band $[G(\vec{k}, \vec{k}') = 1]$.

It is the primary purpose of this paper to modify Eq. (2) in such a way as to make it applicable to the degenerate p-like valence bands.

III. EVALUATION OF $G(\vec{k}, \vec{k}\,')$

Vassell *et al.*[22] have recently shown that, for scattering in the III-V compounds, $G(\vec{k}, \vec{k}\,')$ is conveniently rewritten as

$$G(\vec{k}, \vec{k}\,') = \tfrac{1}{2} \sum_{\mu_1, \mu_2 = \alpha, \beta} \left| \langle \mu_1, \vec{k} \,|\, \mu_2, \vec{k}\,' \rangle \right|^2 , \qquad (3)$$

where R is a rotation operator and the wave functions are those given by Kane[13]

$$\begin{aligned} |i, \alpha, \vec{k}\rangle &= a_i[is\downarrow] + b_i[(x - iy)\uparrow/\sqrt{2}] + c_i[Z\downarrow] , \\ |i, \beta, \vec{k}\rangle &= a_i[is\uparrow] - b_i[(x + iy)\downarrow/\sqrt{2}] + c_i[Z\uparrow] , \\ |1, \alpha, \vec{k}\rangle &= [(x + iy)\uparrow/\sqrt{2}] , \qquad (4) \\ |1, \beta, \vec{k}\rangle &= [(x - iy)\uparrow/\sqrt{2}] , \end{aligned}$$

where 1 refers to the heavy-hole band and i indexes the light-hole, split-off, and conduction bands. These wave functions result from the exact diagonalization of the $\vec{k} \cdot \vec{P}$ and k-independent spin-orbit interaction between the conduction and valence bands. The effects of higher bands have been neglected. (This is often referred to as the "two-band" approximation.) In this approximation the heavy-hole band is not mixed with the other bands and hence remains parabolic and purely p-like. This approximation will be adequate for present purposes provided the effect of higher bands on the heavy-hole band is acknowledged to the extent of assigning an experimentally determined scalar mass m_1^* to that band.

The coefficients a, b, and c are functions of k given by Eq. (15) of Ref. 13. The coefficients for the light-hole band have been calculated for Ge, Si, and the III-V compounds and are shown in Figs. 1–3.[23] The band parameters used in calculating the curves shown in Figs. 1–3 are given in Table I. Following a recommendation of Lawaetz,[24] the momentum matrix element was taken to be $E_p = (2m_0/\hbar^2)P^2 = 25.9$ eV for materials in which both cores of the unit cell have filled d shells (Ge, GaAs, GaSb, InAs, and InSb), 23.2 eV for materials in which only one core contains d electrons (AlAs, AlSb, GaP, and InP), and 20.5 eV for materials in which there are no d electrons (Si and AlP). In the

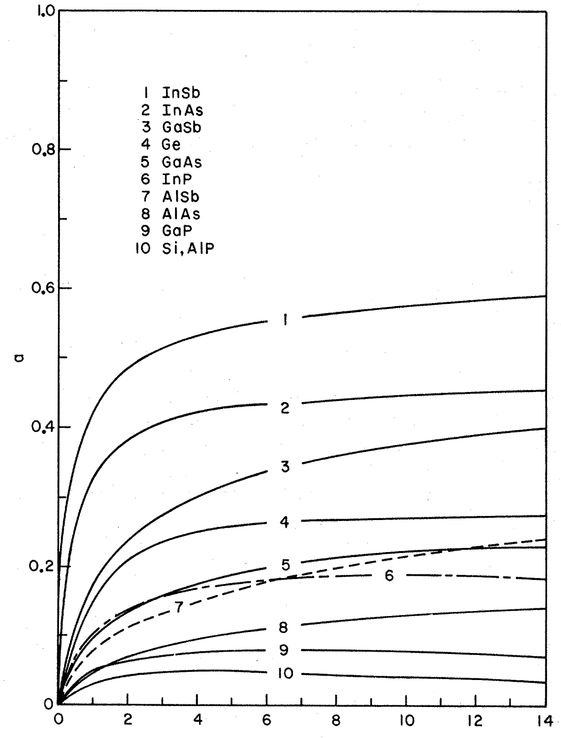

FIG. 1. Wave-function coefficient a for the light-hole band as a function of wave vector squared (k is in units of reciprocal Bohr radii). The coefficient a is a measure of the admixture of s-like symmetry into the light-hole wave functions. At 300 °K the occupied region of the light-hole band extends to $k^2 \approx (2\text{–}4) \times 10^{-4} a_0^{-2}$.

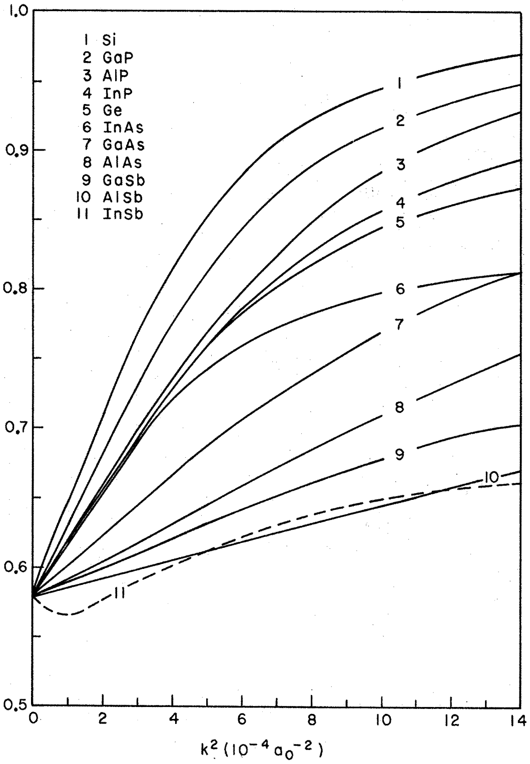

FIG. 2. Wave-function coefficient b for the light-hole band as a function of wave vector squared. Note that $b < 0$ for the light-hole band.

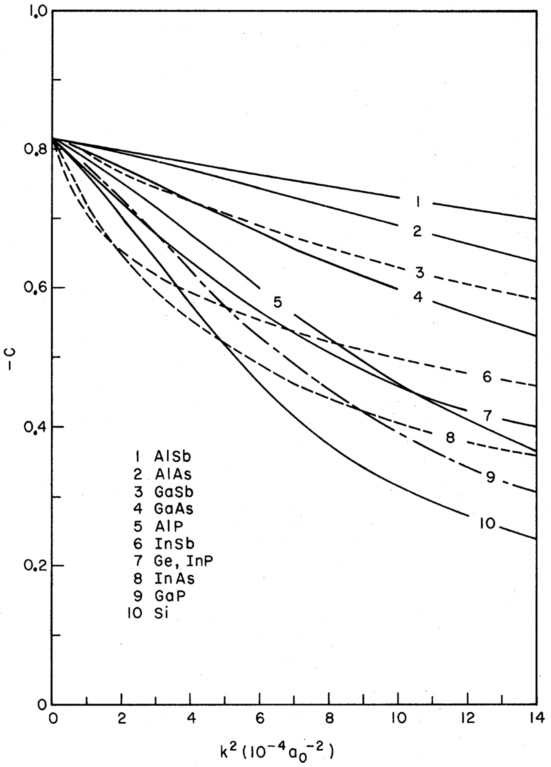

FIG. 3. Wave-function coefficient c for the light-hole band as a function of wave vector squared. Note that $c < 0$ for the light-hole band.

neighborhood of $E_p = 20$ eV, a ±5-eV variation in E_p causes a variation of less than 10% in a, b, and c at $k^2 = 10^{-3} a_0^{-2}$. Kane[13] has given a, b, and c for InSb including the effects of higher bands and using $E_p = 13.5$ eV. As a check on its accuracy, the two-band model was used to calculate a, b, and c for InSb using $E_p = 13.5$ eV and the results were compared with Fig. 2(b) of Ref. 13. The comparison showed the two-band model to be accurate to within 20% for $k^2 = 14 \times 10^{-4} a_0^{-2}$ and much better for smaller k values. This is quite adequate since the room-temperature thermal occupation of the light-hole band corresponds to $k^2 \approx (2\text{–}4) \times 10^{-4} a_0^{-2}$ for these meaterials. Fawcett and Ruch[16] have investigated the effects on *electron* transport of including the higher bands in several III-V compounds. They also concluded that the two-band approximation is adequate.

If the wave functions of Eq. (4) are rewritten in the angular momentum representation $|j_1, j_2; J, M\rangle$ they become

$$
\begin{aligned}
|i, \alpha, \vec{k}\rangle &= i a_k |0, \tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}\rangle + A|1, \tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}\rangle + B|1, \tfrac{1}{2}; \tfrac{3}{2}, -\tfrac{1}{2}\rangle , \\
|i, \beta, \vec{k}\rangle &= i a_k |0, \tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}\rangle - A|1, \tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}\rangle + B|1, \tfrac{1}{2}; \tfrac{3}{2}, \tfrac{1}{2}\rangle , \\
|1, \alpha, \vec{k}\rangle &= |1, \tfrac{1}{2}; \tfrac{3}{2}, \tfrac{3}{2}\rangle , \\
|1, \beta, \vec{k}\rangle &= |1, \tfrac{1}{2}; \tfrac{3}{2}, -\tfrac{3}{2}\rangle , \qquad (5)
\end{aligned}
$$

where $A = (c_i - \sqrt{2}\, b_i)/\sqrt{3}$ and $B = (\sqrt{2}\, c_i + b_i)/\sqrt{3}$. Using these wave functions it can be shown[14,22] that, for *intraband* scattering in the conduction band, light-hole band, and split-off band, $G(\vec{k}, \vec{k}')$ is given by

$$
\begin{aligned}
G_{ii}(\vec{k}, \vec{k}') = {} & a^2(k) a^2(k') + 2a(k)a(k')[b(k)b(k') \\
& + c(k)c(k')] \cos\gamma + [b(k)b(k') + c(k)c(k')]^2 \cos^2\gamma \\
& + \{\tfrac{1}{2} b(k)b(k') - [b(k)c(k') + b(k')c(k)]/\sqrt{2}\}^2 \sin^2\chi , \qquad (6)
\end{aligned}
$$

where γ is the angle between $\vec{k}$ and $\vec{k}'$ and the notation G_{ij} has been introduced to denote scattering from band i to band j. In the present paper, Eq. (6) will be used only for intraband scattering in the light-hole band which will be denoted $G_{22}(\vec{k}, \vec{k}')$.

By using the method described in Ref. 22, it is straightforward to calculate $G(\vec{k}, \vec{k}')$ for intraband scattering in the heavy-hole band, denoted $G_{11}(\vec{k}, \vec{k}')$. The result is

$$G_{11}(\vec{k}, \vec{k}') = \tfrac{1}{4}(1 + 3\cos^2\gamma) . \qquad (7)$$

In obtaining this result it is necessary to use two matrix elements in addition to those given in Ref. 22. These two matrix elements are

$$r^{3/2}_{3/2,3/2}(\theta) = \cos^3 \tfrac{1}{2}\theta$$

and (8)

$$r^{3/2}_{3/2,-3/2}(\theta) = -\sin^3 \tfrac{1}{2}\theta .$$

TABLE I. The zone-center energy gaps and valence-band spin-orbit splittings for Ge, Si, and the III-V compounds. Unless otherwise noted all values were taken from a recent tabulation by Lawaetz (Ref. 24).

Material	E_0(eV)	Δ_0(eV)
Ge	0.89	0.30
Si	4.07	0.04
AlP	5.3[a]	0.06[b]
AlAs	2.9[a]	0.3[b]
AlSb	1.80	0.75
GaP	2.87	0.08
GaAs	1.50	0.35
GaSb	0.81	0.80
InP	1.34	0.21
InAs	0.36	0.43
InSb	0.24	0.90

[a] Calculated using Eq. (3.7) of J. A. Van Vechten, Phys. Rev. 187, 1007 (1969).

[b] Estimated from atomic spin-orbit splittings.

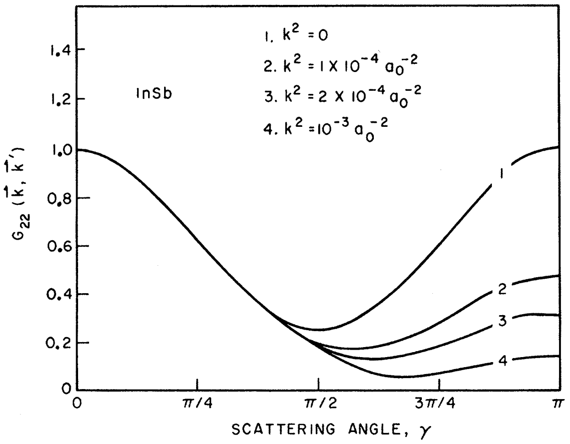

FIG. 4. Overlap function $G_{22}(\vec{k},\vec{k}')$ (intraband scattering for light holes) as a function of the scattering angle γ for various values of k^2 for InSb. Similar curves are obtained for InAs and GaSb. The overlap function for intraband scattering of heavy holes, $G_{11}(\vec{k},\vec{k}')$, is independent of k^2 and is identical to the $k^2=0$ curve shown here. All of the curves were calculated assuming $|k|\approx|k'|$ (elastic limit).

The calculation of $G_{11}(\vec{k},\vec{k}')$ can be performed in full generality ($\vec{k}$ and $\vec{k}'$ at arbitrary angles) or, more simply, by allowing $\vec{k}$ to point along the z axis. The result is the same in either case. Note also that $G_{22}(\vec{k},\vec{k}')$ reduces to the same form as $G_{11}(\vec{k},\vec{k}')$ at $k=0$ where $a=0$, $b=-1/\sqrt{3}$, and $c=-\sqrt{\tfrac{2}{3}}$.

Finally, for transport in the degenerate valence bands one must consider interband scattering. The overlap functions for scattering between the light- and heavy-hole bands are calculated in the same manner as the intraband overlap functions except that each matrix element in Eq. (3) is now evaluated between wave functions corresponding to different bands. The results are

$$G_{12}(\vec{k},\vec{k}')=\tfrac{1}{4}[b(k')+\sqrt{2}\,c(k')]^2\sin^2\gamma$$
and
$$G_{21}(\vec{k},\vec{k}')=\tfrac{1}{4}[b(k)+\sqrt{2}\,c(k)]^2\sin^2\gamma\ . \qquad (9)$$

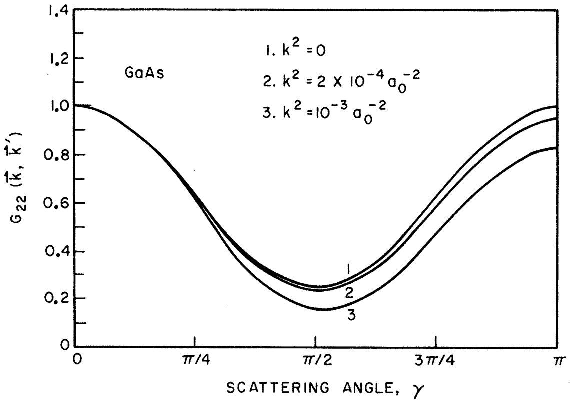

FIG. 5. Similar to Fig. 4. The curves shown here were calculated for GaAs which is representative of the intermediate-gap materials GaAs, Ge, AlSb, and InP.

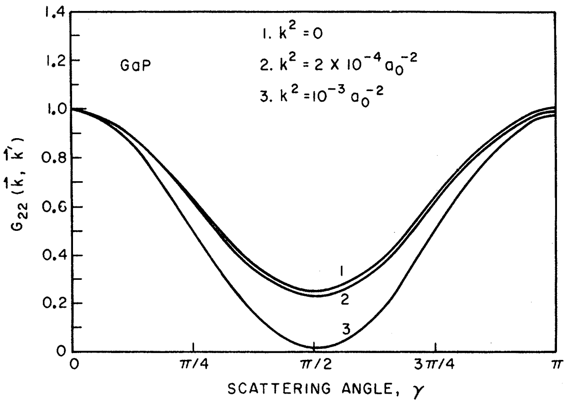

FIG. 6. Similar to Fig. 4. The curves shown here were calculated for GaP which is representative of the wide-gap materials GaP, Si, AlP, and AlAs.

The angular dependence of Eqs. (6), (7), and (9) is shown in Figs. 4–7. Since $G_{11}(\vec{k},\vec{k}')$ is independent of k, its dependence on the scattering angle is always the same and is quite simple (the same as the $k=0$ curve in Figs. 4–6). The behavior of

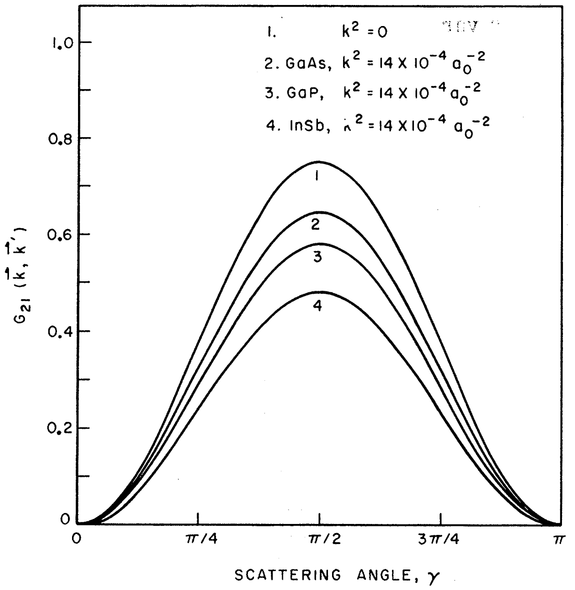

FIG. 7. Overlap function $G_{12}(\vec{k},\vec{k}')$ (interband scattering between the light- and heavy-hole bands) as a function of the scattering angle γ. Note that G_{12} discriminates strongly against small-angle scattering processes (e.g., polar-mode, piezoelectric, and ionized-impurity scattering).

$G_{22}(\vec{k}, \vec{k}')$ is more complicated owing to the k dependence of a, b, and c. If $G_{22}(\vec{k}, \vec{k}')$ is calculated for all the materials listed in Table I, it is found that they fall roughly into three groups according to the size of E_0: (a) InSb, InAs, and GaSb; (b) Ge, GaAs, InP, and AlSb; and (c) Si, GaP, AlP, and AlAs. Within each group the behavior of $G_{22}(\vec{k}, \vec{k}')$ is quite similar for different materials. In Figs. 4–6, $G_{22}(\vec{k}, \vec{k}')$ is plotted as a function of γ for one representative material from each group. In plotting these curves it has been assumed for the sake of simplicity that the scattering is elastic. It is seen that, with the exception of the narrow-gap materials, the deviation of $G_{22}(\vec{k}, \vec{k}')$ from its $k=0$ form is really rather modest. Thus, in the medium- and wide-gap materials it is a good approximation to write

$$G_{22}(\vec{k}, \vec{k}') \approx G_{11}(\vec{k}, \vec{k}') = \tfrac{1}{4}(1+3\cos^2\gamma) \ . \tag{10}$$

In Fig. 7 the interband overlap function is plotted for InSb, GaAs, and GaP. [Again, elastic scattering has been assumed. Note that when $k=k'$, $G_{21}(\vec{k}, \vec{k}') = G_{12}(\vec{k}, \vec{k}')$.] Also plotted in Fig. 7 is the approximation

$$G_{12}(\vec{k}, \vec{k}') = G_{21}(\vec{k}, \vec{k}') \approx \tfrac{3}{4}\sin^2\gamma \ . \tag{11}$$

At $k=0$, Eq. (11) is exact. It is seen from Fig. 7 that Eq. (11) is a fair approximation even for large values of k. One can reach the same conclusion by inspection of Eq. (9) and Figs. 2 and 3.

Before leaving the discussion of the overlap functions it is worthwhile to point out that the equations given for G_{12} and G_{21} [Eq. (9)] are equally valid for scattering between the heavy-hole and split-off bands (G_{13} and G_{31}) provided the coefficients b and c for the split-off band are used. As can be seen from Eq. (15) of Ref. 13, however, b and c have opposite signs for the split-off band. It is easily verified that this causes G_{13} and G_{31} to be quite small even for fairly large values of k. This fact is only relevant for Si, AlP, and GaP since it is only for these materials that Δ_0 is small enough to make the split-off band energetically accessible at high temperatures or high electric fields.

IV. EFFECTS OF $G(\vec{k}, \vec{k}')$ ON HOLE MOBILITY

A. Polar-Mode Scattering

In any attempt to calculate the polar mobility in p-type III-V compounds one encounters two difficulties. One is the inherent difficulty of solving the Boltzmann equation for polar-mode scattering even for a single isolated band,[4,25] and the other is the necessity of considering not one but two (coupled) Boltzmann equations.[17,18] The equations could presumably be solved by techniques similar to those used by Ehrenreich[4,5] (variational) or Rode[26] (iterative) including the appropriate overlap functions. Another method of calculation (which has been used extensively in treating problems of high-field transport) is the Monte Carlo method.[15,16] This method has the advantage of allowing transport problems to be treated in their full complexity but carries with it the disadvantage of reduced physical insight into the problem at hand.

As an alternative to the more rigorous approaches mentioned above, the following simple model is proposed for polar-mode scattering in the p-type III-V compounds. Since the transition probability for polar-mode scattering is proportional[4] to $1/q^2$, where q is the phonon wave vector, the scattering strongly favors small momentum changes ($\vec{k}\approx\vec{k}'$). This, coupled with the $\sin^2\gamma$ dependence of $G_{12}(\vec{k}, \vec{k}')$ means that polar-mode scattering is very ineffective in causing interband transitions since these require large momentum changes. Thus, it is reasonable to consider the light- and heavy-hole bands to be decoupled for polar-mode scattering. The polar mobility can then be calculated separately for each band and combined in a weighted average[27]

$$\mu = (p_1\mu_1 + p_2\mu_2)/(p_1+p_2) \ , \tag{12}$$

where p_1 and p_2 are the concentrations of heavy and light holes, respectively. Through this device the problem is reduced to one of assessing the effects of G_{11} and G_{22} on the polar mobility in isolated bands. This is most easily accomplished for the heavy-hole band by noting that $G_{11}(\vec{k}, \vec{k}')$ depends only on γ and enters the expression for the scattering probability as a multiplicative factor. Thus, $G_{11}(\gamma)$ will reduce the scattering rate by a factor given by

$$\frac{I'}{I} = \int_0^\pi \frac{G_{11}(\gamma)\,(1-\cos\gamma)}{q^2}\,\sin\gamma\,d\gamma \Bigg/ \int_0^\pi \frac{(1-\cos\gamma)}{q^2}\,\sin\gamma\,d\gamma \ , \tag{13}$$

where $q^2 = k^2 + k'^2 - 2kk'\cos\gamma$. The factor $(1-\cos\gamma)$ is a weighting factor which reflects the fact that it is primarily large-angle scattering which impedes the motion of carriers in the direction of the applied field and hence affects the mobility.[28–30] The evaluation of Eq. (13) is given in the Appendix where it is shown that $I'/I = 0.5$ to within 6% for all values of k and k'. Thus the effect of $G_{11}(\gamma)$ is to reduce the scattering rate by a factor of 2 and therefore to increase the polar mobility in the heavy-hole band by a factor of 2 over the value that would have been obtained from Eq. (2).

A similar analysis can be carried through for the light-hole band but the expression for I'/I becomes complicated because of the k dependence of $G_{22}(\vec{k}, \vec{k}')$. In the approximation of Eq. (10), however, the results are identical to those obtained for the heavy-hole band. In this approximation a particularly simple expression can be derived for the total polar mobility as follows. Assuming parabolic bands, the heavy- and light-hole concentrations are related by $p_1/p_2=(m_1^*/m_2^*)^{3/2}$. This, together with the fact that m^* enters Eq. (2) as $(m^*)^{-3/2}$, allows Eq. (12) to be written as

$$\mu_{\mathrm{PO}}=2\frac{2r^{3/2}}{1+r^{3/2}}\,\mu_{\mathrm{PO}}(s,m_1^*)\,, \tag{14}$$

where $r\equiv m_1^*/m_2^*$, and $\mu_{\mathrm{PO}}(s,m_1^*)$ is the polar mobility as calculated for s-like bands [Eq. (2)] using the heavy-hole mass m_1^*. For the III-V compounds the factor containing r lies in the range 1.7–1.9 so that the over-all polar mobility is a factor of 3.4–3.8 larger than previously calculated from Eq. (2).

At high temperatures and for the group of materials with small band gaps, the light-hole overlap function $G_{22}(\vec{k},\vec{k}')$ will cause a greater increase in μ_2 than the factor of 2 estimated above. This effect is not difficult to calculate but it is compensated or exceeded by the decrease in μ caused by the increase in m_1^* and m_2^* with temperature.

Finally, the entire analysis given here for polar-mode scattering applies equally well to piezoelectric scattering since the m^* and q dependence of the scattering probability is the same for both cases. Thus, for piezoelectric scattering in p-type III-V compounds, one should use Eq. (14) with $\mu_{\mathrm{piezo}}(s,m_1^*)$ substituted for $\mu_{\mathrm{PO}}(s,m_1^*)$.

B. Acoustic and NPO Scattering

The complexity of acoustic and NPO scattering in Ge-like valence bands is amply discussed in Refs. 17–21. It suffices to say that one must include the effects of longitudinal and transverse phonons, light and heavy holes, interband scattering, and p-like wave functions. Although these complications require a considerable modification of the deformation-potential theory, the calculated mobility displays the *same temperature dependence* as that obtained for simple bands. This is probably the most important conclusion to be drawn from the rigorous calculations, and it provides justification for using the expression given in I and fitting experimental data with adjustable deformation potentials E_{AC} and E_{NPO} which contain the effects of the above-mentioned complications. Defined in this way, E_{AC} and E_{NPO} already include the effects of the overlap integral $G(\vec{k},\vec{k}')$ and the expression given previously for the acoustic and NPO mobility[7] need not be modified.

C. Comparison with Experiment

In I it was shown that the Hall mobility data of several p-type III-V compounds can be fitted without including any polar-mode scattering. The inclusion of polar-mode scattering will cause a slight decrease in the fitted values of the deformation potentials. As an example, the data for p-GaP[31] have been refitted and the results are shown in Fig. 8. In obtaining this fit the acoustic-mode deformation potential was changed from the previously reported[7] value of 5.7–4.9 eV. Other parameters used were $m_1^*=0.88m_0$, $e^*=0.23e$, $M=3.6\times10^{-23}$ g, $v_a=4.05\times10^{-23}$ cm^3, and $\theta=580$ °K. The total lattice-scattering mobility was obtained by combining μ_{PO} with the combined acoustic and NPO mobility[7] μ_{AO} according to Mathiessen's rule[32]:

$$1/\mu=1/\mu_{\mathrm{PO}}+1/\mu_{\mathrm{AO}}\,. \tag{15}$$

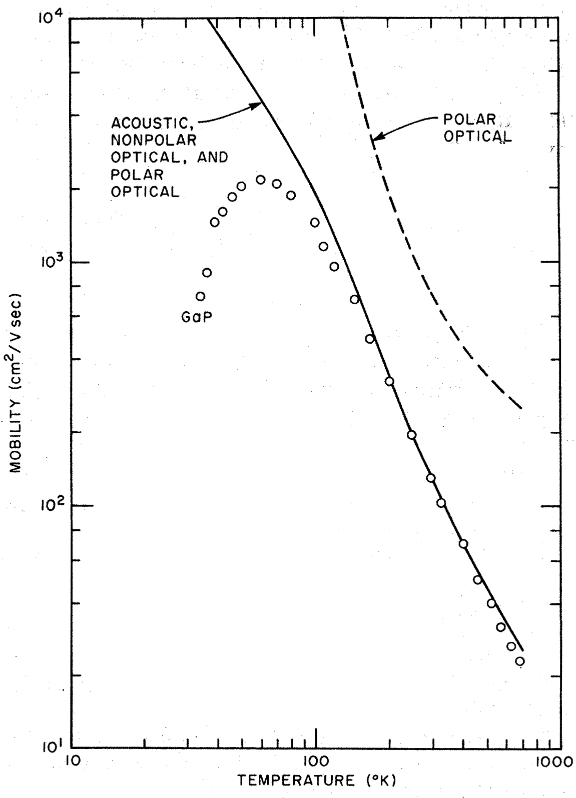

FIG. 8. A revised fit to the data of Casey, Ermanis, and Wolfstirn (Ref. 31). The solid line is the total theoretical lattice-scattering mobility. The dashed curve shows the contribution of polar-mode scattering.

Parameters needed in calculating μ_{AO} are given in I. The only parameter which was adjusted to obtain the fit shown in Fig. 8 was E_{AC}. [The NPO deformation potential was changed in order to keep the ratio $\eta=(E_{\mathrm{NPO}}/E_{\mathrm{AC}})^2$ constant and equal to 4 as discussed in Ref. 7. If E_{AC} and η are considered to be the two adjustable deformation parameters, then E_{AC} was changed and η was not.] In Ref. 8 it was shown that E_{AC} has a calculated value of

3.5–4 eV for most of the III-V compounds. This result was based on values of b and d in the range $b \approx 1.5$ and $d \approx 4.4$ eV. Recent work by Yu *et al.*[33] indicates that these values may be somewhat low. Using their values of b and d, one obtains $E_{AC} = 3.3$, 5.3, and 4.4 eV for Ge, GaAs, and InSb, respectively. Thus, a value of 4.9 eV for GaP seems quite reasonable. In view of the inherent approximations of the model and uncertainties in m_1^*, however, it is unwise to place too much emphasis on this agreement.

V. SUMMARY AND CONCLUSIONS

It has been pointed out that previous calculations of the polar mobility in p-type III-V compounds were incorrect in that they utilized an expression which is valid only for simple s-like bands. For scattering in the valence bands it is necessary to include the effects of Ehrenreich's overlap function $G(\vec{k}, \vec{k}')$ and the presence of a small number of very high-mobility holes in the light-hole band. A physically appealing model was proposed within which these effects lead to a particularly simple expression for the polar mobility [Eq. (14)]. It was shown that μ_{PO} is a factor of 3.4–3.8 larger than previously calculated. This explains why it was possible in I to fit experimental data for several p-type materials without including any polar-mode scattering. The relative importance of acoustic-, NPO-, and polar-mode scattering will vary slightly from material to material but it now appears that the nonpolar scattering mechanisms (acoustic and NPO) are dominant in all the p-type III-V compounds.

Although Eq. (14) is certainly to be preferred over Eq. (2) for application to p-type materials, the present model obviously contains several approximations which require further justification. Work is in progress to compare the model with results obtained by iterative solution of the Boltzmann equation.

ACKNOWLEDGMENTS

I should like to thank E. O. Kane for a very helpful discussion of the valence-band wave functions and their approximation in III-V compounds. I am also indebted to P. Lawaetz for several helpful observations and comments. Assistance in numerical calculations and computer programming was provided by J. A. Seman.

APPENDIX

Letting $s = 2kk'/(k^2 + k'^2)$ and $x = \cos\gamma$, it is straightforward to perform the integrations indicated in Eq. (13). The transformed integrals are

$$I = \frac{1}{k^2 + k'^2} \int_{-1}^{1} \frac{(1-x)\,dx}{1 - sx} \tag{A1}$$

and

$$I' = \frac{1}{4}\left(I - \frac{1}{k^2 + k'^2} \int_{-1}^{1} \frac{3x^2(1-x)\,dx}{1 - sx} \right) . \tag{A2}$$

The resulting expression for I'/I is given by

$$\frac{I'}{I} = \frac{1}{4} + \frac{3}{4}\left(\frac{s^{-4}[2s - 2s^2 + 2s^3/3 + (s-1)\ln|(1+s)/(1-s)|]}{s^{-2}[2s + (s-1)\ln|(1+s)/(1-s)|]} \right) . \tag{A3}$$

In the limiting cases of $s \to 1$ (elastic limit) and $s \to 0$ (extreme inelasticity) $I'/I \to \frac{1}{2}$. By calculation for intermediate values of s, it is found that I'/I reaches a minimum value of 0.47 at $s \approx 0.5$. In considering the limiting cases it is necessary to keep several terms in the expansions for the log terms since considerable cancellation occurs.

---

[1] C. Hilsum and A. C. Rose-Innes, *Semiconducting III-V Compounds* (Pergamon, New York, 1961).

[2] O. Madelung, *Physics of III-V Compounds* (Wiley, New York, 1964).

[3] C. Hilsum, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), Vol. 1.

[4] H. Ehrenreich, J. Phys. Chem. Solids 2, 131 (1957); 9, 129 (1959).

[5] H. Ehrenreich, J. Phys. Chem. Solids 8, 130 (1959).

[6] Unless otherwise indicated, references to "Ehrenreich's expression for polar mobility" or "the usual expression for polar mobility" are meant to indicate Eq. (10) of Ref. 5.

[7] J. D. Wiley and M. DiDomenico, Jr., Phys. Rev. B 2, 427 (1970); 2, 5074 (1970).

[8] J. D. Wiley, Solid State Commun. 8, 1865 (1970).

[9] M. Costato and L. Reggiani, Nuovo Cimento Letters 4, 848 (1970).

[10] D. M. Brown and R. Bray, Phys. Rev. 127, 1593 (1962).

[11] As will be seen shortly, Ehrenreich's initial formulation of the problem of polar-mode scattering (Ref. 4) is more general than the final expression which he derives for n-InSb. The latter expression has since been applied to cases for which it was not intended.

[12] The overlap function appears variously in the literature as $\mathcal{G}_{\pm}(\beta)$, $\mathcal{G}(k, k', y)$, $\mathcal{G}$, $G(\gamma)$, and $G(\vec{k}, \vec{k}')$.

[13] E. O. Kane, J. Phys. Chem. Solids 1, 249 (1957).

[14] D. Matz, J. Phys. Chem. Solids 28, 373 (1967); Phys. Rev. 168, 843 (1968).

[15] W. Fawcett, A. D. Boardman, and S. Swain, J.

Phys. Chem. Solids 31, 1963 (1970).

[16] W. Fawcett and J. G. Ruch (unpublished).

[17] H. Ehrenreich and A. W. Overhauser, Phys. Rev. 104, 331 (1956); 104, 649 (1956).

[18] G. I. Bir, E. Normantas, and G. E. Pikus, Fiz. Tverd. Tela 4, 1180 (1962) [Sov. Phys. Solid State 4, 867 (1962)].

[19] G. D. Whitfield, Phys. Rev. Letters 2, 204 (1959); Phys. Rev. 121, 720 (1961).

[20] M. Tiersten, IBM J. Res. Develop. 5, 122 (1961); J. Phys. Chem. Solids 25, 1151 (1964).

[21] P. Lawaetz, Phys. Rev. 174, 867 (1968); see also 166, 763 (1968); 183, 730 (1969); Phys. Status Solidi 11, K117 (1965).

[22] M. O. Vassell, A. K. Ganguly, and E. M. Conwell, Phys. Rev. B 2, 948 (1970).

[23] Note that, in evaluating Eq. (15) of Ref. 13, one must use the exact roots of the secular equation and not the approximate expressions which are valid only for very small k.

[24] P. Lawaetz, Phys. Rev. (to be published).

[25] D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) A219, 53 (1953).

[26] D. L. Rode, Phys. Rev. B 2, 1012 (1970).

[27] This approach has also been suggested for ionized impurity scattering by H. Brooks, *Advances in Electronics and Electron Physics* (Academic, New York, 1955), Vol. 7.

[28] E. M. Conwell, *High Field Transport in Semiconductors* (Academic, New York, 1967), Chap. V, Sec. I.

[29] F. J. Blatt, *Physics of Electronic Conduction in Solids* (McGraw-Hill, New York, 1968), p. 125.

[30] The use of Eq. (13) implicitly assumes the existence of a relaxation time. This is a convenience which is only justified at high temperatures where the scattering becomes more nearly elastic.

[31] H. C. Casey, F. Ermanis, and K. B. Wolfstirn, J. Appl. Phys. 40, 2945 (1969).

[32] The error caused by using this approximation will be small since μ_{PO} makes only a small contribution to the total mobility.

[33] P. Y. Yu, M. Cardona, and F. H. Pollak, Phys. Rev. B 3, 340 (1971).

PHYSICAL REVIEW B VOLUME 4, NUMBER 8 15 OCTOBER 1971

Temperature Dependence of the Long-Wavelength Optical Phonons in Diamond*

E. Anastassakis, H. C. Hwang, and C. H. Perry
Department of Physics, Northeastern University, Boston, Massachusetts 02115

(Received 21 June 1971)

We investigate the effects of temperature in the range 10–1000 °K on the frequency and linewidth of the $\vec{q} \simeq 0$ optical phonons in diamond, using Raman-scattering techniques. Comparison is made between the present results and those obtained experimentally and theoretically by other workers. As the temperature increases, the broadening of the line is determined by an increasing number of channels through which the mode decays into pairs of acoustical modes. Beyond 850 °K it is found that the crystal exhibits higher-order anharmonicity. It is also established that the frequency shift is largely due to thermal expansion, and that the scattering occurs under conditions of phonon-population equilibrium.

I. INTRODUCTION

Diamond exhibits one triply degenerate long-wavelength optical mode (referred to as "mode" from now on) which is Raman active and normally infrared (ir) inactive. The mode is a strong scatterer and its frequency has been well established through Raman-scattering techniques for a long time.[1] The frequency has also been confirmed by neutron[2] and ir experiments.[3] The study of the temperature dependence of Raman-scattering spectra of silicon[4] and germanium,[5] the other two common diamond-type crystals, has led to interesting conclusions regarding the anharmonicity of these crystals, and the validity of the existing lattice-dynamical theoretical models.[6,7] A similar study of the temperature dependence of the Raman spectrum of diamond, mainly in first order, was made by Krishnan[1] long before any theoretical work had been attempted. A complete account of the temperature dependence of diamond's second-order Raman spectra below 300 °K was recently reported by Solin and Ramdas.[8]

We report in this paper our most recent results of the investigation of the temperature dependence of diamond's first-order Raman scattering, in the range 10–1000 °K. The differences between the present results and those obtained by Krishnan appear to be relatively small. However, the improved Raman experimental data indicate that the applicability of the existing theoretical models needs to be reexamined as the agreement between theory and experiment can be considered only as partially satisfactory.

II. EXPERIMENTAL

The measurements were taken using a Spex-1401 double-grating spectrometer and photocounting techniques. The type-IIa diamond sample was kindly supplied by the S. Africa Diamond Research