Role of Phonons in the Oscillatory Photoconductivity Spectrum of Semiconducting Diamond

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The oscillatory photoconductivity spectrum associated with the acceptor center in semiconducting diamond has been measured over the spectral energy range 0.35–2.6 eV (3.5–0.47 μ). The energy separation between the acceptor ground state and the top of the valence band is more than twice the longitudinal optical (LO) phonon energy, and the spectrum is interpreted in terms of hole capture from the valence band to *excited states* of the acceptor center together with the cascade emission of one or more optical phonons. Transitions involving the emission of up to 14 phonons have been detected. The mean phonon energy in the cascade process is *not* constant, as has been generally assumed, but decreases gradually as the number of phonons involved increases. This is shown to be consistent with the curvature of the valence band and the dispersion curves for LO phonons. In addition, features have been observed in the photoconductivity spectrum which are considered to be due to the phonon-assisted hole capture to excited states of the acceptor center for which transitions from the ground state are forbidden, and which therefore have not previously been observed in absorption measurements on natural semiconducting diamond.

I. INTRODUCTION

OSCILLATIONS in the photoconductivity continua associated with donor or acceptor impurities have been reported for a number of semiconductors,[1] and different authors have suggested various mechanisms which might give rise to the observed phenomena. Benoit à la Guillaume and Cernogora[2] and Engeler, Levinstein, and Stannard[3] explain the minima in the photoresponse curves for germanium and indium antimonide, respectively, as being due to the *superposition* of several spectra spaced by the energy of the k=0 longitudinal optical (LO) phonon. Essentially, if we consider the optical excitation of a *p*-type semiconductor, then, starting at the threshold at k=0 and going to higher energies, the photoresponse first increases with the increasing density of states in the valence band, and then decreases because of the rapidly decreasing transition probability as further excursions into k space are involved. However, when a photon energy is reached where a LO phonon can be emitted, the transitions can again take place at k=0, and the process is repeated with the emission of this phonon. Hence a spectrum is obtained with a series of minima spaced by the energy of the LO phonon. If this interpretation were correct, then a similar behavior should be observed in the absorption spectrum since the optical absorption constant is directly related to the over-all transition probability discussed above. However, Kurova and Ormont[4] and

Besfamil'naya *et al.*[5] point out that there are no oscillations in the absorption spectrum of germanium and conclude that the above mechanism is unlikely. Besfamil'naya *et al.* attribute the photoconductivity structure as due to a lifetime modulation effect, previously suggested by Stocker *et al.*[6] A hole at the top of the valence band can be rapidly captured by an impurity center. From deeper in the band the hole must *first* lose energy by interaction with acoustic phonons; however, if the energy of the hole below the top of the valence band is a multiple of the optical-phonon energy, it can lose this energy very rapidly ($<10^{-12}$ sec in InSb)[7] by cascade emission of optical phonons. Thus the photoconductive response will exhibit minima at energies which are equal to the separation of the ground state of the impurity from the valence band plus a multiple of the LO phonon energy, since for these energies many holes are captured from the valence band before they can contribute to the photocurrent. This process will not affect the absorption significantly and no absorption oscillations should occur.

Various other models have been put forward, both for the case of transitions from impurity bound states and for valence- to conduction-band transitions in direct-gap semiconductors (see Ref. 1), but are not thought to be relevant here. Following their earlier measurements on InSb,[6] Stocker *et al.*[1] have since shown that oscillatory structure in the photoconductivity spectrum may occur without the presence of a trapping center, at least for direct transitions where the carriers

[1] A summary of such measurements is given by H. J. Stocker, H. Levinstein, and C. R. Stannard, Phys. Rev. **150**, 613 (1966).

[2] C. Benoit à la Guillaume and J. Cernogora, J. Phys. Chem. Solids **24**, 383 (1963).

[3] E. Engeler, H. Levinstein, and C. Stannard, Phys. Rev. Letters **7**, 62 (1961).

[4] I. A. Kurova and N. N. Ormont, Fiz. Tverd. Tela **6**, 3708 (1964) [English transl.: Soviet Phys.—Solid State **6**, 2970 (1964)].

[5] V. A. Besfamil'naya, I. A. Kurova, N. N. Ormont, and V. V. Ostroborodova, Zh. Eksperim. i Teor. Fiz. **48**, 1588 (1965) [English transl.: Soviet Phys.—JETP **21**, 1065 (1965)].

[6] H. Stocker, C. Stannard, I. Kaplan, and H. Levinstein, Phys. Rev. Letters **12**, 163 (1964).

[7] M. A. Habeggar and H. Y. Fan, Phys. Rev. Letters **12**, 99 (1964).

photoexcited by monochromatic radiation are mono-energetic, e.g., direct band-to-band transitions and impurity-to-band transitions. Their mechanism is operative only at very low temperatures, where it may be assumed that the steady-state energy distribution of the photoexcited carriers is far from thermal equilibrium. They conclude that the oscillations in the photoconductivity are produced by the influence of the external electric field on this nonequilibrium energy distribution. This implies that the photocurrent must be a nonlinear function of applied voltage when the oscillations occur.

The mechanism responsible for the oscillatory photoconductivity in semiconducting diamond appears to be similar to the lifetime modulation interpretation put forward by Stocker et al.[6] and subsequent workers, but the situation is complicated by the fact that the ionization energy of the acceptor impurity is rather greater than twice the energy of the Raman ($k=0$) phonon, whereas in other materials it is usually very much smaller. The experimental evidence suggests that the hole is captured, not from the valence-band edge to the acceptor ground state, but from (presumably "labeled") energy levels in the valence band to the excited states of the acceptor, these levels being lower in energy from the relevant excited state by exactly the energy of the $k=0$ LO phonon. This mechanism was first suggested for diamond by Hardy et al.[8] and subsequently by Ruffino and Charette.[9] Neither, however, extended their measurements sufficiently far to explain certain energy discrepancies in the positions of peaks arising from the multiphonon cascade process described above. Earlier measurements in this laboratory[10] indicated that the phonon energy involved, averaged over ten "oscillations," was 161 rather than 165 meV, the energy of the Raman phonon. The measurements to be described in this paper show that the mean energy of the phonon involved in the multiphonon cascade process is not constant, but decreases gradually as the number of phonons involved increases. This is because when a large number of phonons is taking part the entire cascade process cannot be considered as taking place at or near $k=0$, and the variation of the LO phonon energy with k must be taken into account.

A further feature of this hole-capture process by excited states is that holes can be captured from the valence band by excited states to which optical transitions from the ground state are forbidden. Thus certain minima in the one-phonon region of the photoconductivity spectrum have been identified with excited states which have not previously been observed in the absorption spectrum. One of these minima, in particular, has

been associated with an excited state at 0.266 eV to which optical transitions are normally forbidden but which was theoretically predicted by Smith and Taylor[11] and has actually been observed in heavily doped synthetic semiconducting diamond.[12]

The absorption spectrum of semiconducting diamond is characterized by a continuum absorption starting at about 0.37 eV and extending into the visible to about 2.2 eV, and the early part of this continuum has absorption maxima superimposed on it at 0.462, 0.508, 0.625, and 0.67 eV. Three prominent bands are observed at energies below the continuum threshold at 0.304, 0.348, and 0.363 eV, which, if examined at low temperature with high resolution, exhibit a considerable amount of fine structure. Wedepohl[13] has measured the intensities of these peaks and also the absorption in the continuum at selected wavelengths for six different diamonds and found a very good correlation between them, which indicated that they were all associated with the same center. After a detailed examination of these features Smith and Taylor[11] concluded that those below 0.37 eV were due to transitions of bound holes between the ground state and various excited states of the acceptor center. The peaks superimposed on the continuum were considered to be bound hole transitions of the acceptor center with the emission of one or more lattice phonons of energy 0.159 eV. Smith and Taylor refer to these as "phonon-assisted" transitions, and the process is peculiar to substances like diamond in which the impurity activation energy is substantially larger than the Raman energy. According to Hardy et al.,[8] the probability of observing the nth multiphonon-assisted transition in absorption is proportional to $E^*/(E^*+nE_p)$, where E^* is the energy of the excited state and E_p the energy of the phonon. Thus we see that in silicon and germanium the process is an unlikely one, and that, even in diamond, the probability becomes small after the second or third phonon-assisted transition. Smith and Taylor also pointed out that the absorption spectrum shows a step at 0.16 eV from its fundamental edge. This effect is not pronounced but is clearly discernible, and is presumably due to the superposition of spectra in accordance with the mechanism of Engeler et al.[3] described earlier.

Therefore, in semiconducting diamond, we have three types of phonon processes operative simultaneously. (We have previously shown that there is no effect with electric field except for a slight broadening of the spectrum for fields greater than 1.5 kV/cm.[14]) In the absorption spectrum we have evidence of the superposition of spectra, although the effect is not a strong one and, even if present in photoconductivity, is masked by much

[8] J. R. Hardy, S. D. Smith, and W. Taylor, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter 1962,* edited by A. C. Stickland (The Institute of Physics and the Physical Society, London, 1962), p. 521.

[9] G. Ruffino and J. J. Charette, Ricerca Sci. **36,** 526 (1966).

[10] E. C. Lightowlers, A. T. Collins, P. Denham, and P. S. Walsh, Ind. Diamond Rev. Suppl. **28,** 11 (1968).

[11] S. D. Smith and W. Taylor, Proc. Phys. Soc. (London) **79,** 1142 (1962).

[12] A. T. Collins, P. J. Dean, E. C. Lightowlers, and W. F. Sherman, Phys. Rev. **140,** A1272 (1965).

[13] P. T. Wedepohl, Proc. Phys. Soc. (London) **70B,** 177 (1957).

[14] A. T. Collins and E. C. Lightowlers, Phys. Rev. **171,** 843 (1968).

more prominent features. In addition, the phonon-assisted absorption may cause a slight reduction in photoconductivity, but even in the one-phonon–assisted absorption the increase in absorption is much less than the decrease in photoconductivity due to the hole-capture mechanism described below. Finally, in the photoconductivity spectrum a large number of features appear which are associated with hole capture from the valence band in conjunction with the multiphonon cascade process. This process does not affect the absorption spectrum, and is the one on which we wish to concentrate in this paper.

II. EXPERIMENTAL

Measurements have been made on a number of natural and synthetic semiconducting diamonds, and the typical results reported here were obtained using a natural diamond SA65C polished into a rectangular parallelepiped approximately $3 \times 1 \times 1$mm. Two electrodes were electron-beam-welded to one surface using a gold-tantalum-aluminum alloy (90% Au, 9% Ta, 1% Al) giving mechanically strong, electrically stable, Ohmic contacts. The diamond was mounted on the copper nose piece of a conventional metal cryostat using G. E. low-temperature varnish and a thin layer of mica for insulation; the insulation between the diamond and the cold finger was $> 10^{12} \, \Omega$. The cryostat was fitted with a CaF_2 window, and all measurements were made at liquid-nitrogen temperature.

The optical and electrical arrangement was similar to that described previously,[14] the final chart-recorder output being the ratio of the signal obtained from the diamond to that of a thermocouple detector which was assumed to have uniform sensitivity over the spectral region of interest. In addition, because of the wide wavelength range covered, the quartz-envelope tungsten-iodine lamp used as the source was servocontrolled so that the radiant energy emerging from the exit slits of the monochromator was maintained approximately constant at all wavelengths.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the photoconductivity response in the region where transitions involving hole capture to the excited states occur with emission of one, two, or three phonons, and has been observed with varying degrees of precision by a number of authors.[8,9,15] The single peak d at 468 meV is approximately 165 meV higher than the lowest energy peak in the absorption spectrum at 304 meV. The band at e has been measured at high resolution by Hardy et al.[8] and Ruffino and Charette,[9] and also at liquid-helium temperature by the present authors,[14] and contains over a dozen components which are 165 meV higher in energy than corresponding struc-

[15] J. B. Krumme and W. G. Leivo, J. Appl. Phys. 38, 3879 (1967).
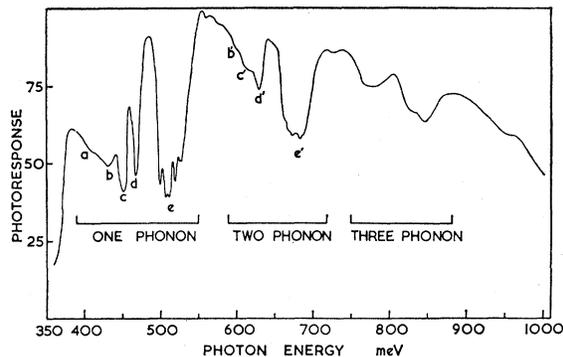
FIG. 1. Detailed photoconductivity structure in the one-, two-, and three-phonon region. The band e' is the two-phonon replica of the band e, and so on.

ture in the absorption spectrum. To the minima a–c, however, there are no corresponding features in the absorption spectrum. The minimum c has also been observed by Ruffino and Charette, and Hardy et al. show minima similar to b and c in their diagram, but do not refer to them in the text. We feel that the minima a–c on the photoconductivity continuum are due to hole capture, with the emission of one phonon, by excited states of the acceptor center to which transitions from the ground state are forbidden, and so are not normally detected in absorption measurements. This view is reinforced by the fact that, in order to explain the anomalously large width of the absorption peak at 0.304 eV, Smith and Taylor[11] calculated that there must be a forbidden transition at about 0.266 eV. This normally forbidden transition has been observed in the absorption spectrum of heavily doped synthetic semiconducting diamond in which some mixing of states is introduced by the very high impurity concentration.[12] The minimum at b occurs at 431 meV, which is clearly $266+165$, and this tends to confirm the ideas outlined above. It does not therefore seem unreasonable to associate the minima a and c with two other excited states at 0.24 and 0.289 eV, respectively, to which transitions from the ground state are forbidden.

The transitions involving only one phonon take place close to $\mathbf{k}=0$ because the acceptor excited state is relatively effective masslike, so that the wave function of the bound hole is concentrated in a narrow range of $\mathbf{k}$ around $\mathbf{k}=0$. The spread in the energy of the optical phonon near $\mathbf{k}=0$ is small, and therefore well-resolved spectral structure occurs in the one-phonon region. There is, however, an underlying band in this region presumably associated with contributions from the full phonon spectrum when momentum can be conserved by the recoil of the acceptor ion. When two or more phonons, and larger and larger excursions into $\mathbf{k}$ space, are involved, the phonon energy becomes less well defined and coupling to fine structure in the absorption spectrum is less apparent. Thus, in the two-phonon region in Fig. 1, b', c', and d' are barely resolved; there
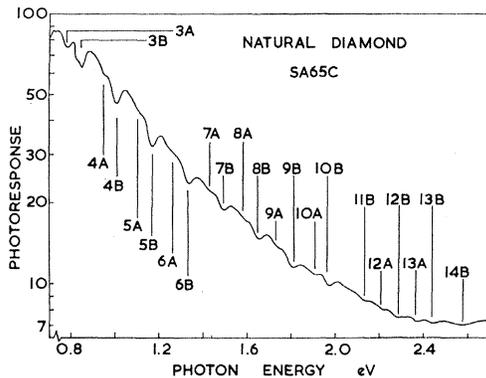
FIG. 2. Minima associated with the multiphonon cascade process. Peaks labeled nA result from hole capture to the 0.304-eV excited state and nB to the 0.348-eV state, where n is the number of phonons involved. It will be observed that the ordinate axis is logarithmic.

is no feature a' and the band e' is almost devoid of fine structure. In the three-phonon region the replicas of b', c', and d' have run together to form one band at about 785 meV, and the replica of e' is even broader. We can therefore label these, and subsequent multiphonon bands shown in Fig. 2, by nA and nB, where n represents the number of phonons and A and B the lower- and higher-energy replica coupled back to the 0.304- and 0.348-eV excited states, respectively. The energies of the B features, which are the stronger throughout, have been carefully measured from the original charts and are plotted in Fig. 3 against the number of phonons involved. Careful inspection of Fig. 3 will show that the points lie, not on a straight line, but on a gentle continuous curve. The experimental points have been fitted with the quadratic curve

$$E = 347.5 + 167.0n - 0.53n^2 \text{ meV},$$
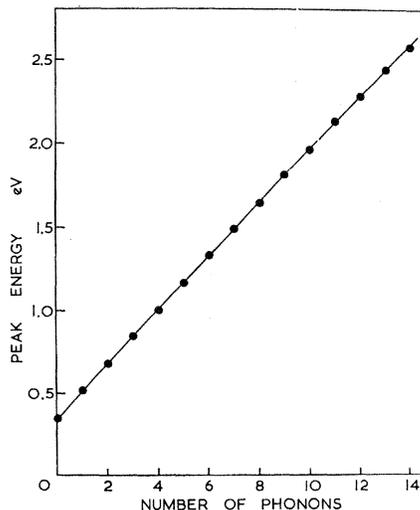
FIG. 3. Energies of the B features of Figs. 1 and 2 plotted against the number of phonons. Note that the experimental points lie on a gentle curve.

which suggests that the phonon energy for the first transition is 166.0 meV, and decreases by approximately 1 meV per phonon thereafter. An alternative estimate can be obtained by plotting the *separation* of consecutive peaks against the number of phonons. The experimental scatter is inevitably large, but such a plot is shown in Fig. 4, together with the computed best straight-line fit which indicates that the $n=1$ phonon energy is 164 meV and that it decreases by about $\frac{3}{4}$ meV per phonon. It will further be observed from Fig. 4 that the *average* phonon energy taken over ten transitions is 160.5 meV. This agrees well with the value obtained in an earlier series of less accurate measurements on synthetic semiconducting diamond[10] when it was assumed that the phonon energy was *constant*. There, data similar to Fig. 3, but more scattered and taken over only ten phonons, were fitted to a straight line of slope 161 meV. The present work, however, shows that the phonon energy is equal to the Raman energy for the one-phonon transition and then decreases gradually in value as more and more phonons are involved. A plausible explanation for this is given in Figs. 5 and 6. For the sake of simplicity we shall consider in Fig. 5 the situation for which the constant-energy surfaces in
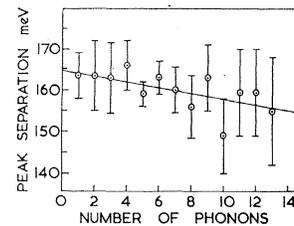
FIG. 4. Energy separation of successive B features in Figs. 1 and 2 plotted against phonon number, and the computed best straight-line fit.

k space are spheres. The lower part of Fig. 5 schematically represents the E-k diagram for the valence band in which E is plotted against k_x, an arbitrary component of **k**. The upper diagram represents some corresponding constant-energy circles in two-dimensional **k** space.

In the lower diagram consider first the one-phonon transition. The hole is excited from the ground state at 1 to the labeled level, and is immediately captured by the excited state from a representative point such as C. Now consider the two-phonon transition. The hole is excited from 2 to the point A on the E-k diagram; it must then change energy *and* momentum to reach the labeled level. The minimum change in momentum $\Delta k_{\min(2)}$ is incurred on going to the point B on the E-k diagram, and the maximum change $\Delta k_{\max(2)}$ in going to the point C on the E-k diagram diametrically opposite B. Intermediate values of Δk can be represented by the transition to a point such as D in the upper diagram. In fact, the transition can take place to any point on the surface of constant energy in three-dimensional **k** space

(which is difficult to represent diagrammatically) and the hole will undergo a change in momentum somewhere between $\Delta k_{\min(2)}$ and $\Delta k_{\max(2)}$ which we will denote by some average value $\langle \Delta k(2) \rangle$. If we now consider the twelve-phonon transition, we see by analogy that in the *first* step of the cascade emission of phonons the hole loses momentum $\langle \Delta k(12) \rangle$, in the second step $\langle \Delta k(11) \rangle$, etc. Tentatively, one might suggest that $\langle \Delta k(i) \rangle$ is given by $\frac{1}{2}(\Delta k_{\min(i)} + \Delta k_{\max(i)})$, but exactly how the average is formed is immaterial; clearly $\langle \Delta k(n+1) \rangle$ is greater than $\langle \Delta k(n) \rangle$. We must now consider the ω-k dispersion curve for the LO phonon shown in Fig. 6. Again this must be a rather schematic representation, since it is an average over all crystallographic directions. What can be said with certainty is that at $k = 0$, $\omega = \omega_R$, the Raman frequency, and that ω decreases as $k \rightarrow k_{\max}$.[16] Hence we see that the frequency (or energy) of "high-momentum" phonons is lower than that of the low-momentum phonons, perhaps by as much as about 7% at $k = k_{\max}$. Recent band-structure calculations for diamond suggest that the valence band is about 2 eV lower at $k = k_{\max}$ than at $k = 0$ in the $\langle 111 \rangle$ directions.[17] The spectral range covered in these experiments is just about 2 eV, and so one would expect, using the above interpretation, that the mean energy of the phonon participating in the cascade emission process would change from 165 meV for the one-phonon transition to ~ 155 meV in the highest transition—exactly as observed experimentally.

IV. SUMMARY AND CONCLUSIONS

The minima in the photoconductivity continuum for semiconducting diamond have been interpreted as being due to the rapid capture of photoexcited holes from the valence band to one or other of the two excited states of the acceptor center which are most prominent in the absorption spectrum, together with the emission of one or more LO phonons. The ionization energy of the acceptor center is 0.373 eV [14]; in the absorption spectrum the first of the excited states appears as a featureless band at 0.304 eV and the second as a band centered at 0.348 eV which exhibits considerable fine structure.[11] When only one phonon is emitted in the photoconductivity process, this fine structure is reproduced as a series of minima superimposed on a broad underlying band. The fine structure arises because the wave function of the bound hole is localized near $k = 0$, where the spread in the energy of the LO phonon is small, and corresponding features in the absorption and photoconductivity spectra will be separated by 165 meV, the energy of the Raman phonon. However, because momentum of the acceptor ion can be conserved by recoil, there will, in addition, be an underlying

[16] J. L. Warren, J. L. Yarnell, G. Dolling, and R. A. Cowley, Phys. Rev. **158**, 805 (1967).
[17] F. Herman, R. L. Kortum, C. D. Kuglin, and R. A. Short, J. Phys. Soc. Japan Suppl. **21**, 7 (1966).
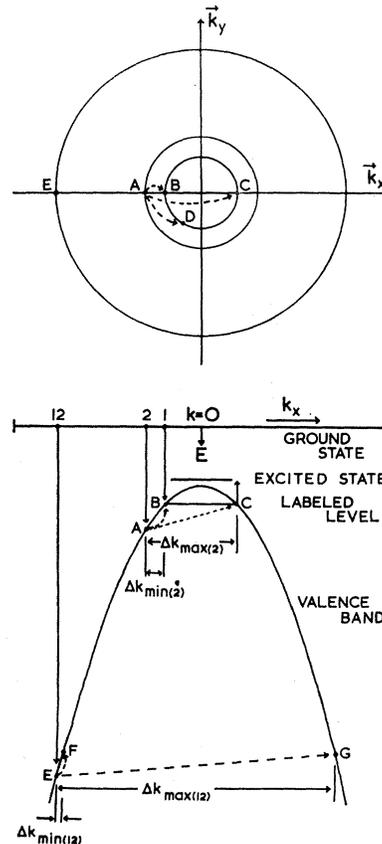
FIG. 5. The lower figure schematically represents the E-k diagram for the valence band, and the upper figure the constant-energy circles in two-dimensional $\mathbf{k}$ space. The lower diagram shows that the average change in hole momentum when a phonon is emitted becomes larger the more deeply the hole is excited into the valence band.

contribution from the full phonon spectrum. Our conclusions thus far are in complete agreement with Hardy *et al.*[8] and Ruffino and Charette.[9] As we have previously indicated,[14] the analysis of similar data by Krumme and Leivo[15] in terms of five activation energies and three discrete phonon energies seriously conflicts with the model of the acceptor center in semiconducting diamond which has been firmly established by a number of authors over the past twelve years.
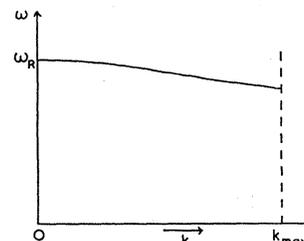
FIG. 6. Schematic ω-k diagram averaged over all crystal directions representing the change in frequency of the LO phonon with increasing k.

When more than one phonon is emitted in a cascade process, however, the phonon energy becomes less precise, and the transition takes place further from $k=0$. We have shown by a qualitative argument, taking into consideration the curvature of the valence band and the dispersion curves for the LO phonon, that the energy spacing of the higher-energy minima will gradually decrease, and that fine structure will no longer be discernible when several phonons are emitted in cascade. This is borne out exactly by our experimental measurements.

Finally, certain features which are observed in the one-phonon region of the photoconductivity spectrum are considered to be due to hole capture, with the emission of one phonon, to excited states of the acceptor center to which transitions from the ground state are forbidden. This interpretation is reinforced by the fact that the energy of one of these forbidden transitions is in good agreement with other theoretical and experimental evidence.

Long-Wavelength Phonon Scattering in Nonpolar Semiconductors

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The long-wavelength acoustic- and optical-phonon scattering of carriers in nonpolar semiconductors is considered from a general point of view. The deformation-potential approximation is defined and it is shown that long-range electrostatic forces give a nontrivial correction to the scattering. For completeness, corrections due to nonlocal effects like spin-orbit coupling are treated, but the general conclusion is that the deformation-potential approach is a very good approximation except in some cases of optical-phonon scattering. The smallness of the nontrivial corrections is interpreted in terms of the very-short-range nature of interactions in a covalent semiconductor.

I. INTRODUCTION

IT has recently been suggested that the usual deformation-potential theory may be inadequate for the description of long-wavelength phonon scattering in p-type Ge.[1] Before that, theoretical investigations of the phonon spectrum in Ge had shown[2] that long-range forces of quadrupole nature are needed for the interpretation of the experimental data. Tolpygo[3] found that these electrostatic forces also give a nontrivial contribution to the electron-phonon interaction, and a quantitative estimate[4] for Ge indicated that the effect may be of the same order of magnitude as that derived from deformation-potential theory.

In order to study this and other possible shortcomings of deformation-potential theory, we shall begin in Sec. II by establishing the theoretical background of this model of the interaction between carriers and long-wavelength acoustic phonons. The long-range interaction is then introduced in Sec. III and Tolpygo's results[3] are rederived, but on a new and more general basis, and new features arise as a consequence of the combined treatment.

After these general considerations, we shall be concerned quantitatively in Sec. IV with the electrostatic contribution to the long-wavelength acoustic scattering in Ge. In the case of electrons, the new terms are readily incorporated in the theory of Herring and Vogt,[5] and it is shown that the new theory may be consistent with experimental data if the effect is of the estimated magnitude or even somewhat larger. For

[1] P. Lawaetz, Phys. Rev. **174**, 867 (1968).

[2] M. Lax, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 179. This paper contains references to earlier work on the theory of the phonon spectra in nonpolar semiconductors.

[3] K. B. Tolpygo, Fiz. Tverd. Tela **4**, 1765 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1297 (1963)].

[4] Z. A. Demidenko and K. B. Tolpygo, Fiz. Tverd. Tela **6**, 3321 (1964) [English transl.: Soviet Phys.—Solid State **6**, 2656 (1965)].

[5] C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).