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Two-photon absorption in Ge: Band effects

Garnett W. Bryant
Department of Physics, Washington State University, Pullman, Washington 99164
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Calculations are reported of the two-photon absorption in germanium using a Kane band model. All bands within 10 eV of the valence-band edge are considered. The matrix elements are evaluated using $\vec{k}\cdot\vec{p}$ theory to find the relevant wave functions. The spherical model of Baldereschi and Lipari is used to treat the distinction between the light-hole and heavy-hole bands properly. Detailed calculations are made to test various approximations that simplify the evaluation of these complicated nonlinear optical coefficients. For Ge it is essential that the split-off band be included as an intermediate state and that the nonparabolicity of the conduction band be treated correctly. The results of the most complete calculation are in good agreement with experimental results.

I. INTRODUCTION

With the advent of high-intensity lasers, the study of multiphoton transitions has become increasingly more important. Because the selection rules for single and multiphoton transitions are different, each provides different information on a material's band structure. Multiphoton transitions also provide another avenue for studying exciton effects. Furthermore, the study of these processes aids in the understanding and description of the propagation of intense electromagnetic fields through nonlinear materials.

In this paper we present a theoretical study of the two-photon absorption in germanium. There are two important reasons for studying Ge. First, the experimental results for Ge are not extensive and those that are available are not consistent. Zubov *et al.*[1] measured the two-photon absorption coefficient K_2 at 2.36 μm and found it to be 1 cm/MW. Wenzel *et al.*[2] found that K_2 was 2.5 cm/MW near 2.7 μm. This result is inconsistent with the more recent results of Gibson *et al.*[3] for the wavelength range from 2.65 to 3.0 μm. They found that K_2 is less than 0.75 cm/MW throughout this region and is only 0.50 cm/MW at 2.7 μm. Gibson *et al.* were one of the first to eliminate the contribution made to the measured total absorption by those carriers generated in the two-photon absorption process. Consequently, they extracted two-photon absorption coefficients that were lower than the previously measured total absorption coefficients. Gibson *et al.* also reanalyzed earlier data[4,5] for InSb using their more detailed interpretation of the data. Their results were again several orders of magnitude lower than the previous experimental and theoretical[5] estimates. However, more recent results[6] suggest that Gibson's results for InSb are too low because the conduction electron density of the InSb samples was sufficiently high for electrons to fill the conduction-band states needed for the two-photon absorption. We expect this effect to be far less important in Ge with a band gap five times larger than in InSb. Consequently the Gibson results should be the most reliable available for Ge.

The second reason for considering Ge is that it has not been studied theoretically as much as the zinc-blende semiconductors.[5,7,8] Only Arifzhanov and Ivchenko[9] have considered Ge in detail. They provided a group-theoretical analysis of the expression for K_2 but gave no explicit results for K_2. Ge has not been extensively studied for several reasons. For other semiconductors one can often make the approximation that the splitting Δ between the valence and split-off band edges is either much greater or smaller than the energy gap E_c between conduction and valence bands. Such approximations greatly simplify the matrix elements that must be calculated. However, in Ge $\Delta \sim \frac{1}{3}E_c$. Furthermore, for the zinc-blende semiconductors one can choose basis states so that the matrix elements involving states with wave vector $\vec{k}$ transform simply when considering states with different wave vectors. Due to the symmetry of the conduction basis states in Ge (they have the symmetry Γ_2^- rather than Γ_1^+) this is not possible. These two complications make the evaluation of matrix elements and the summation over intermediate states more difficult to perform for Ge.

In Sec. II we present the calculations of K_2. We consider only direct two-photon transitions in Ge. Near threshold a hole is created in the heavy-hole (hh) or light-hold (lh) valence bands and an electron fills a state in the lowest conduction band (c). For higher photon energies we also consider transitions where a hole in the split-off (so) band is created. Two-photon absorption is a two-step process. We thus consider all transitions where the intermediate state is one of the above states or a state in the next highest conduction band (uc, the Γ_{15}^- band). These bands are shown in Fig. 1. In each case,

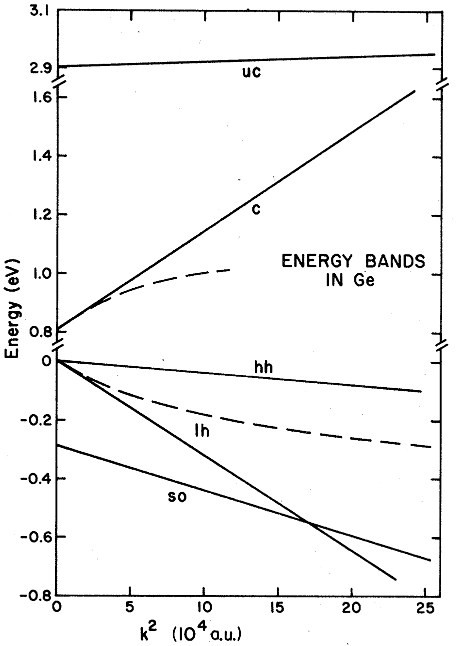

FIG. 1. Band structure of Ge including light-hole (lh), heavy-hole (hh), split-off (so), conduction (c), and upper conduction (uc) bands. The solid curves give the effective-mass approximation. The dashed curves are more realistic approximations for the lh and c bands.

one step is allowed (does not vanish for states at the center of the band) and the other is forbidden (vanishes at the center of the band). There are no allowed-allowed transitions in Ge. By including the bands mentioned, we consider all possible transitions involving intermediate states within 10 eV of the valence edge. We use the spherical model of Baldereschi and Lipari[10] to describe the valence states. This allows us to include their degeneracy properly but not their anisotropy. For comparison we also perform the calculations assuming that the heavy- and light-hole bands are degenerate and can be described by a single effective mass. This permits us to determine the contribution of the valence-band structure to the results. Finally we study the effect of going beyond the effective-mass approximation for the energy bands. This was done recently for the zinc-blende semiconductors,[6] and large increases in K_2 resulted when nonparabolic bands were used.

In Sec. III we present the results. When all of the contributions are included properly we obtain results which are 25% lower then Gibson's results. In view of the uncertainties in the experimental results and in some of the parameters used, this agreement is quite satisfactory. Exciton effects ignored in the simple-band model do not appear to make as large a contribution as suggested by Lee and Fan for the zinc-blende semiconductors. We present final conclusions in Sec. IV.

II. THEORY

For light with a frequency ω and polarization $\vec{\eta}$, the two-photon transition rate is given in second-order perturbation theory by

$$T=\frac{2\pi}{\hbar}\left(\frac{4\pi^2 e^4 I^2}{\epsilon c^2 \omega^4 m^4}\right)\sum_{c,v}\int\frac{d^3k}{(2\pi)^3}\left|\sum_J\frac{\langle c|\vec{\eta}\cdot\vec{\mathrm{p}}|J\rangle\langle J|\vec{\eta}\cdot\vec{\mathrm{p}}|v\rangle}{\epsilon_J(\vec{\mathrm{k}})-\epsilon_v(\vec{\mathrm{k}})-\hbar\omega}\right|^2\delta(2\hbar\omega-\epsilon_c(\vec{\mathrm{k}})-\epsilon_v(\vec{\mathrm{k}}))\,. \tag{1}$$

We do not consider exciton effects[11,12] in this paper so the states in Eq. (1) refer to single-particle band states with energies $\epsilon_\alpha(\vec{\mathrm{k}})$. The sums are over valence and conduction states involved as initial and final states and over intermediate states J. Since we have direct dipole transitions, $\vec{\mathrm{k}}$ denotes the wave vector of the states $|c\rangle$, $|v\rangle$, and $|J\rangle$ involved in the transition. I is the beam intensity, ϵ the dielectric function, and m the free-electron mass. The two-photon absorption coefficient K_2 is given by

$$K_2=2\hbar\omega\, T/I^2\,. \tag{2}$$

We assume that the beam is randomly polarized. Thus our final results are averaged over all possible polarizations.

We use $\vec{\mathrm{k}}\cdot\vec{\mathrm{p}}$ perturbation theory to describe the wave functions to first order in k. This is necessary because the forbidden steps of the two-step transitions are described by the first-order corrections to the wave functions. The basis states for the perturbation theory are those at $k=0$. We use the basis set of Fawcett.[13] The matrix elements of Eq. (1) and those needed in the $\vec{\mathrm{k}}\cdot\vec{\mathrm{p}}$ theory are evaluated using the experimentally determined matrix elements[13] $P=0.6909\ \hbar^2/ma_0$ and $Q=0.5622\ \hbar^2/ma_0$. The real c and so bands remain doubly degenerate for $k\neq 0$. We also treat the uc bands as if they remain degenerate since their contribution to K_2 is small. As a result, the changes in the c, so, and uc wave functions for $k\neq 0$ can be found using standard first-order perturbation theory. The energies are given in the effective-mass approximation by second-order perturbation theory. To second order the c and so bands remain degenerate as they should but the uc bands split. As mentioned, we ignore this splitting by assuming a single uc effective mass. In Table I

TABLE I. Energy gaps E_α and effective masses m_α of electron states in the conduction (c) and upper conduction (uc) bands and of holes in the heavy-hole (hh), light-hole (lh), and split-off (so) bands. Energies are measured relative to the valence-band maximum and are in eV.

α	so	lh	hh	c	uc
E_α	0.29	0.00	0.00	0.805	2.9
m_α/m	0.09	0.042	0.33	0.04	0.64

we list the effective masses and energy gaps.

The degeneracy of the lh and hh states is also lifted for $k \neq 0$. This cannot be ignored as it was for the uc band since the valence states are the initial states of the absorption process. Consequently, we apply second-order degenerate perturbation theory to find the correct combinations of valence basis states that lift the degeneracy for each $\vec{k} \neq 0$. When this is done the energy bands are no longer spherically symmetric. This makes the evaluation of Eq. (1) extremely complicated. To simplify the calculation we use the spherical model of Baldereschi and Lipari[10] to find the valence states. In this model the degeneracy of the valence bands is accounted for, but the energies are no longer anisotropic.

In the spherical model the effective Hamiltonian of second-order degenerate perturbation theory is written

$$H = -\alpha k^2 - \xi(\vec{k}\cdot\vec{J})^2, \quad \alpha > -\tfrac{9}{4}\xi > 0 \tag{3}$$

when terms which lead to the anistropy are ignored. $\vec{J}$ is the spin operator for a spin-$\frac{3}{2}$ system. The valence basis states $|v_i)$, $i = 1$ to 4, that lift the degeneracy when, for example, $\vec{k} = k\hat{z}$ can be written in terms of Fawcett's states. In this representation J_z is diagonal and the states ($i = 1, 4$) for $J_z = \pm\frac{3}{2}$ correspond to the heavy-hole states while the $J_z = \pm\frac{1}{2}$ states are the light-hole states. For $\vec{k} \neq k\hat{z}$, H is diagonalized by a rotation. If θ is the angle between $\vec{k}$ and $\hat{z}$ and ϕ is the azimuthal angle, then H is put in diagonal form $U_\theta U_\phi H U_{-\phi} U_{-\theta}$ by the rotation operators $U_\theta = \exp(i\theta J_y)$ and $U_\phi = \exp(i\phi J_z)$ which diagonalize the component of $\vec{J}$ parallel to $\vec{k}$. The new basis states $|v_j\hat{k})$ which lift the degeneracy for wave vectors in the direction $\hat{k}$ are given by rotating the basis states for $\hat{k} = \hat{z}$:

$$|v_j\hat{k}) = \sum_{i=1}^{4} |v_i)(U_{-\phi}U_{-\theta})_{ij}\,, \tag{4}$$

where $j = 1, 4$ for the heavy-hole states and is 2 or 3 for the light-hole states. Once the appropriate choice of basis states for a particular direction of $\vec{k}$ has been made, the valence wave functions, including the first-order correction which contributes to the momentum matrix elements, are given by standard $\vec{k}\cdot\vec{p}$ theory

$$|v_i\vec{k}) = |v_i\hat{k}) + \sum_\beta \frac{|\beta)(\beta|\hbar\vec{k}\cdot\vec{p}/m|v_i\hat{k})}{-\epsilon_\beta}\,, \tag{5}$$

where the sum is over the c, uc, and so basis states. In this model the energy is again given by the effective-mass approximation. The effective masses are given in Table I.

When we use the effective-mass energies the kinetic energy of the electron-hole pair created by the two-photon absorption is $\epsilon_{cv} = \hbar^2 k^2/2\mu_{cv}$, where $1/\mu_{cv} = 1/m_c + 1/m_v$ and m_c and m_v are the effective masses of the conduction band and a particular valence band. We then get the usual $(\epsilon_{cv})^{1/2}$ for the density of electron-hole states. Since the amplitude for the two-step process is proportional to k, the transition rate from a particular valence band will depend on k^3. The value of k is fixed by energy conservation and gives a transition rate proportional to $(\mu_{cv})^{5/2}(2\hbar\omega - E_c)^{3/2}$. Because $(\mu_{chh})^{5/2}$ is four times larger than $(\mu_{clh})^{5/2}$, the hh band should be much more important in the absorption process. Consequently, it is important that we treat the distinction between the two valence bands accurately.

We also consider the effect of using realistic energy bands. The lower dashed curve of Fig. 1 actually gives a better description of the lh band, as inspection of Fawcett's results[13] shows. This band does not intersect the so band as the effective-mass approximation does and the apparent effective mass is larger. Consequently, the use of the more realistic lh energy band should increase the contribution of the lh band to the transition rate. A study of Fawcett's results also shows that the conduction band is nonparabolic. However, the modification he calculated does not appear to be as large for the c band as for the lh band. Calculations will show, however, that the inclusion of the nonparabolicity of the conduction band in the evaluation of transition rates is more crucial than a proper treatment of the lh band.

To obtain a *simple* analytic expression for a realistic lh band for use in these calculations, we assume that it has the form

$$\epsilon_{lh}(k) = -\frac{\hbar^2 k^2}{2m_{lh}} + \left[(\Delta E)^2 + \left(\frac{\hbar^2 k^2}{2\Delta m_{lh}}\right)^2\right]^{1/2} - \Delta E. \tag{6}$$

The factor $\Delta E(\Delta m_{lh})^2$ was determined by requiring that Eq. (6) give the same k^4 correction as obtained from fourth-order perturbation theory. The other constraint applied to determine ΔE and Δm_{lh} was that the new band have the same slope at large k as the hh band. Thus $1/m_{lh} - 1/\Delta m_{lh} = 1/m_{hh}$. This constraint is arbitrary but an inspection of the bands calculated by Fawcett shows that it is reasonable. We find that $\Delta E = 0.2337$ eV and $\Delta m_{\text{lh}} = 0.0481m$. The results are given as the lower dashed curve of Fig. 1.

We have not attempted to determine an analytic expression for a realistic c band that would be valid over the entire range of k in Fig. 1. Detailed comparisons of calculated K_2 with Gibson's results are only possible for $\hbar\omega$ within 0.07 eV of the threshold. Moreover, it is not clear what the appropriate simple form should be. However, in the energy range near threshold the following expression is valid:

$$\epsilon_c(k) = \frac{\hbar^2 k^2}{2m}\left(\frac{m}{m_c} + \Delta m_c (ka_0)^2\right). \tag{7}$$

We use the effective mass of Table I for m_c and Fawcett's value $\Delta m_c = -1.1\times10^4$ as an estimate for the coefficient of the k^4 term. At large k Eq. (7) is no longer valid because it overestimates the increase in the effective mass and ϵ_c decreases for increasing k. Even for $(ka_0)^2$ greater than 5×10^4, the bending of the band shown in Fig. 1 is probably too extreme. However, the comparisons we make with the experimental values will test electron states for $(ka_0)^2$ only up to 4.5×10^4. In this range we expect Eq. (7) to be an adequate estimate for the mass enhancement.

A comment should be made about the parameters used. The room-temperature energy gaps[14] are used because the data of Gibson were taken at room temperature. An average energy is used for the uc band gap because we ignore the splitting of the uc band. The effective masses do not appear to be temperature dependent. For example, the effective mass of the conduction band is $0.04m$ at both 1.5 K (Ref. 15) and 300 K.[16] Averages of existing experimental masses[14,17,18] are used for m_{so}, m_{lh}, m_{hh}, and m_{uc}. Unfortunately, the value of P that we use is not consistent with $m_c = 0.04m$ if we assume that the second-order perturbation result for ϵ_c gives the correct effective mass

$$\frac{m}{m_c} = 1 + \frac{2P^2 m}{3\hbar^2}\left(\frac{2}{E_c} + \frac{1}{E_c+\Delta}\right). \tag{8}$$

This expression gives $m_c = 0.034m$ if $P = 0.6909\ \hbar^2/ma_0$ and the room-temperature energy gaps are used. A value of $P = 0.624\ \hbar^2/ma_0^2$ must be used to give $m_c = 0.04m$ using Eq. (8). This value of P is significantly lower than those found experimentally.[13,17] We perform calculations with this new value for P and for $m_c = 0.034m$ to test the importance of the uncertainties in these parameters.

Actually evaluating the sums in Eq. (1) is extremely cumbersome because a large number of terms are included when the wave functions are found to first order in $\vec{k}\cdot\vec{p}$ theory. Although the sum over conduction states in Eq. (1) is easily done because the spin-up and spin-down states make the same contribution, the sum over valence states and the intermediate-state sum are difficult to perform. To proceed, we perform the intermediate state sum for fixed c and v. When we integrate over all directions of $\vec{k}$ and average over $\vec{\eta}$, only certain terms of the intermediate-state sum make contributions. These terms are evaluated numerically and their contribution to the transition rate determined. The sum over v is also done numerically. No analytic expression is given for T because it would be very lengthy and not enlightening. Instead, the final results are given in Figs. 2 and 3. There are several techniques which make the evaluation of the sums easier. These are discussed briefly in the Appendix.

III. RESULTS

All of the results presented in Figs. 2 and 3 were found by including the contributions of all bands mentioned as intermediate states and by making the proper distinction between lh and hh states. The solid curve of Fig. 2 was found by using the effective-mass approximation for the bands and by ignoring the k dependence of the energy denominators in Eq. (1). Similar calculations were performed to test the importance of uc and so bands as intermediate states. When the first was ignored K_2 decreased by ten to twenty percent

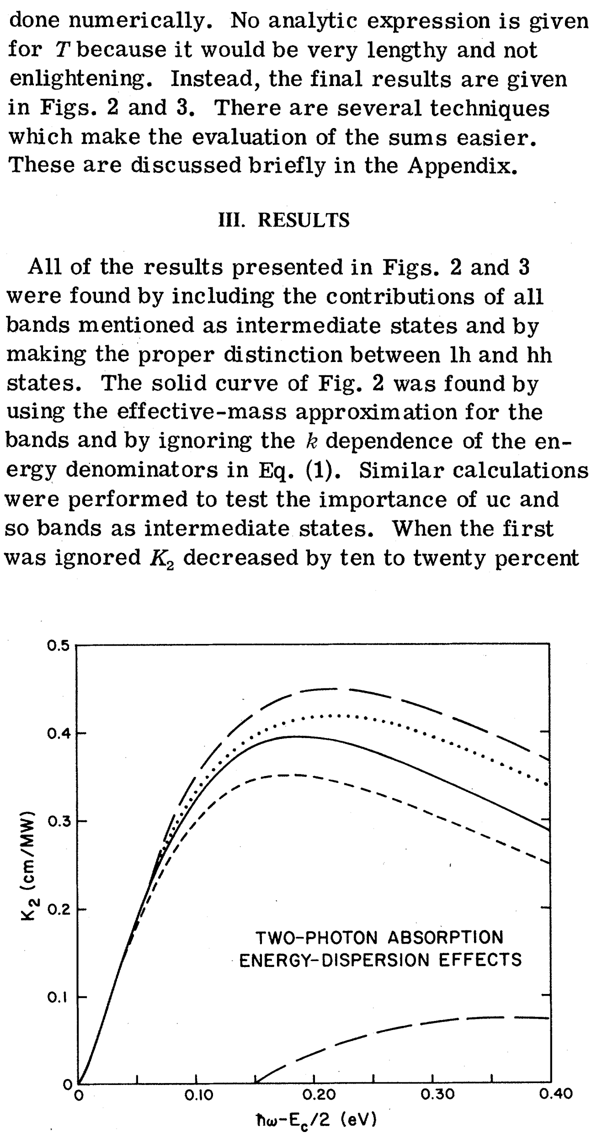

FIG. 2. Energy-dispersion effects on two-photon absorption. The solid curve is calculated by including all bands but by ignoring the k dependence of the energy denominators and by using the effective-mass approximation. The short dashed curve includes the k dependence of the denominators, the long dashed curve uses the realistic lh band. The dotted curve includes both effects. The lower dashed curve is the absorption from the so band including both effects.

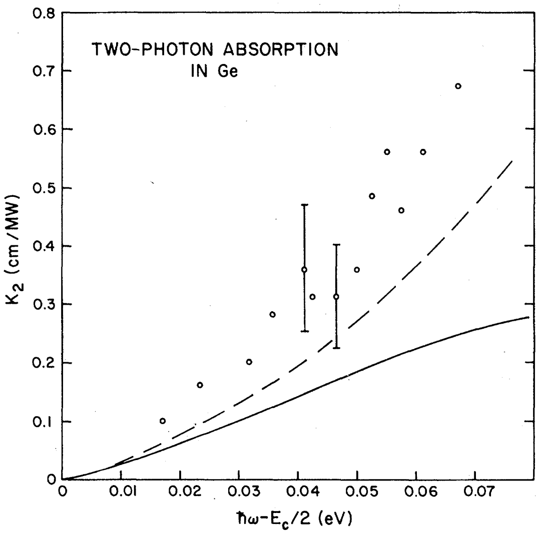

FIG. 3. Comparison of the experimental results of Gibson (Ref. 3) with the simple band-model predictions. The solid curve is found considering all effects except the use of the realistic *c* band. The dashed curve is found using the realistic *c* band. The error bars are taken from Gibson's work.

over the energy range shown in Fig. 2. However, when both bands were ignored, K_2 dropped by a factor of 2. Ignoring the so band is equivalent to assuming that $\Delta \gg E_c, \hbar\omega$. Since $\Delta \sim \frac{1}{3}E_c$, this approximation should not be valid in Ge. Although ignoring the so band is a good approximation for some zinc-blende semiconductors[6] it is a very poor approximation for Ge.

Another calculation was made to determine the importance of including the distinction between lh and hh states. When they are assumed to remain degenerate, the calculation of K_2 is straightforward because the same valence basis states can be used for all directions of $\vec{k}$. There is then no need to use the spherical model to find new basis states for each direction of $\vec{k}$. When the lh and hh bands are treated as degenerate we can replace the $u_{cv}^{5/2}$ factor in the transition rate by either $\frac{1}{2}(\mu_{chh}^{5/2} + \mu_{clh}^{5/2})$ or $[\frac{1}{2}(\mu_{chh} + \mu_{clh})]^{5/2}$. In the first case the results are 6% less than the solid curve and in the second case, 15% less. Thus, if we make a fortuitous choice for an average $\mu_{cv}^{5/2}$ (i.e., we do not replace it with $\mu_{chh}^{5/2}$ or $\mu_{clh}^{5/2}$), then ignoring the distinction between lh and hh bands does not crucially affect K_2.

In Fig. 2 we show the effect of including the *k* dependence in the energy denominators (in the manner discussed in the Appendix) and of using the realistic energy band for the light holes. As expected, these contributions are only important away from the threshold. In the energy range considered, the corrections are only fifteen percent. Including the *k* dependence of the denominators lowers the results. Using a more realistic lh band increases the contribution of the lh band because the lh density of states and the *k* in the matrix element increase. The effects of including the *k* dependence of the denominators and using the realistic lh band compete against each other. A calculation which includes both differs little from one which includes neither in the energy range up to 0.2 eV above threshold. Also shown in Fig. 2 is the absorption coefficient for transitions starting from the so band. The shape is similar to that of the other absorption coefficients. The transition rate is lower because the density of so states is lower than that of hh states. The increase in energy gap also decreases the transition rate.

Different values of P and m_c were used to test their effect on K_2. Specifically, one calculation was made with m_c reduced to $0.034m$ and another with $P = 0.624\ \hbar^2/ma_0$. In these calculations the *k* dependence of the energy denominators was included and the realistic lh band was used. The new values of P and m_c are too low to be reliable; but, as mentioned, they are needed if Eq. (8) is to give an m_c consistent with the P used. Since the absorption coefficient scales very roughly as P^2 and as $m_c^{5/2}$, K_2 decreases when the new parameters are used. In fact, it decreases by 35% for the new value of P and by 20% for the new value of m_c. However, the uncertainty in K_2 should not be as large as this suggests since the actual uncertainty in P and m_c should be much less.

A comparison between the experimental results of Gibson[3] and the calculation that includes the realistic lh band, the *k* dependence of the denominators, standard parameters, and the distinction between lh and hh bands is shown in Fig. 3. Our comparison is limited because no data are available for $\hbar\omega$ more than 0.07 eV from the threshold. Obviously, even when the uncertainty in the data is considered, the predictions are too low by a factor of about 2. The agreement is adequate near threshold but gets worse 0.05 eV beyond the threshold. The more rapid rise beyond 0.05 eV is not predicted by the calculation using the simple *c* band. However, when the nonparabolic conduction band is used, a large enhancement of the calculated absorption occurs. In view of the uncertainty in the experimental results, the parameters used and the approximations made, the agreement between this calculation and the experimental results is quite satisfactory. Most importantly, the more rapid rise in K_2 at higher energies is evident. This occurs because the apparent effective mass of the *c* band increases for increasing *k*. This effect of the nonparabolicity of the *c* band is especially important for two-photon absorption which scales roughly as the $\frac{5}{2}$ power of the apparent effective conduction mass rather than as the $\frac{3}{2}$ power as in single-photon absorption. Consequently, the two-photon absorption should more readily reveal the contribution of the nonparabolicity. This is apparent from Fig. 3. Because we do not determine a realistic c band valid for large k, we do not determine the shape or magnitude of the absorption coefficient at large energies.

Zubov[1] measured K_2 at 2.36 μm to be 1.0 em/MW. At this energy (0.518 eV) we predict K_2 to be only 0.4 cm/MW when we use the effective-mass approximation. However, Zubov obtained the experimental value without correcting for the generated carrier absorption. As Gibson has shown, this leads to K_2 values which are too large. Moreover, use of the nonparabolic c band can increase the calculated absorption coefficient by more than a factor of 2 for $\hbar\omega$ greater than 0.05 eV from threshold. Thus the simple band model should be consistent with Zubov's result provided that realistic bands are used.

We should note that no attempt has been made to include higher-order corrections to the matrix elements, even though it is apparent that higher-order corrections to the effective masses are significant. Unfortunately too many terms would have to be evaluated to make inclusion of these higher-order corrections feasible.

IV. CONCLUSIONS

We have presented a simple band-model calculation of the two-photon absorption in Ge. The calculation treats the degeneracy of the valence bands correctly and includes all allowed transitions involving states within 10 eV of the valence edge. In addition, the k dependence of the energy denominators is treated approximately but adequately and realistic energy bands for c and lh states are used. When all of these contributions are included, the agreement between our results and Gibson's results is good. The two effects which must be included to obtain reliable results are the use of the realistic c energy band and the use of the so band as an intermediate state. The other approximations, ignoring the k dependence of the denominators, ignoring the distinction between lh and hh bands and ignoring the uc band, are all more reasonable.

Several effects have not been considered in the simple band model. No attempt has been made to include exciton effects as done by Lee and Fan.[5] The good agreement that we get with Gibson's results suggests that this effect should be small. Lee and Fan find a large enhancement for some zinc-blende semiconductors when exciton effects are considered. For example, the exciton effects increase the absorption in ZnTe by a factor of 10 and in GaAs by a factor of 2. In these materials the lowest exciton has a binding energy of 10 and 4.4 meV, respectively, while in Ge it has an energy of only 1.6 meV.[19] For this reason we would further expect exciton effects to be less important in Ge.

The effect on the band states of the intense fields needed to measure two-photon absorption has been ignored. Keldysh[20] originally studied the effect of an intense field on electronic transitions. When this theory was applied to two-photon transitions,[21] the results were typically a factor of 10 lower than measured values and were lower than those calculated with the band model of Basov. Thus it would appear that inclusion of the Keldysh effect would lower our results and worsen the agreement. Although the simple band model appears to be adequate for Ge, the importance of exciton and high-field effects cannot be ruled out. These effects require further consideration.

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APPENDIX

We must consider the following operator

$$M_v=\sum_J \frac{\vec{\eta}\cdot\vec{p}\,|J\rangle\langle J|\,\vec{\eta}\cdot\vec{p}}{\epsilon_J(k)-\epsilon_v(k)-\hbar\omega}\,. \tag{A1}$$

To determine T, we calculate

$$\sum_v \langle c|M_v|v\rangle\langle v|M_v|c\rangle\,. \tag{A2}$$

We evaluate M_v for two simplified cases. In the first case we ignore the k dependence of the energy denominators, using only the energy gaps to evaluate $\epsilon_J(k)-\epsilon_v(k)$. In this case M_v is the same for lh and hh states. Moreover, in the intermediate-state sum, the sum over lh and hh can be done by ignoring the distinction between lh and hh states when the denominator is the same for both. The same valence basis states can then be used for each wave vector.

We also evaluate M_v with the k dependence of the denominator included. In this case M_{lh} and M_{hh} are different. However, in the sum over J the sum over lh and hh can only be done simply if the difference in the two bands is still ignored. Thus we make the following approximation:

$$\sum_{J\in \mathrm{lh},\mathrm{hh}} \frac{\vec{\eta}\cdot\vec{\mathrm{p}}\,|J\rangle\langle J|\,\vec{\eta}\cdot\vec{\mathrm{p}}}{\epsilon_J(k)-\epsilon_v(k)-\hbar\omega} \simeq \tfrac{1}{2}\Big(\sum_{J\in \mathrm{lh},\mathrm{hh}} \vec{\eta}\cdot\vec{\mathrm{p}}|J\rangle\langle J|\vec{\eta}\cdot\vec{\mathrm{p}}\Big) \times\left(\frac{1}{\epsilon_{\mathrm{lh}}(k)-\epsilon_v(k)-\hbar\omega}+\frac{1}{\epsilon_{\mathrm{hh}}(k)-\epsilon_v(k)-\hbar\omega}\right). \tag{A3}$$

The results for K_2 found using Eq. (A3) do not differ greatly from those found when the k dependence is ignored altogether. Thus we expect Eq. (A3) to give an adequate approximation for the k dependence.

There are several ways to make the evaluation of Eq. (A2) easier. First note that

$$\sum_{v\in \mathrm{hh}} |\langle c|M_{\mathrm{hh}}|v\rangle|^2 = \sum_{v\in \mathrm{lh},\,\mathrm{hh}} |\langle c|M_{\mathrm{hh}}|v\rangle|^2 - \sum_{v\in \mathrm{lh}} |\langle c|M_{\mathrm{hh}}|v\rangle|^2 . \tag{A4}$$

As argued before, when we sum over all lh and hh states and the operator is the same for both, we can ignore the difference in lh and hh states and use the simpler valence basis states. Thus the first term in Eq. (A4) is easier to evaluate. In the second sum we must use the lh states found using the basis states given by Eqs. (4) and (5). However, this sum is easier to perform than the original one over hh states. To see this we need to consider the following.

The matrix operators U_ϕ and U_θ take the following form[22]:

$$U_\phi = \begin{pmatrix} e^{i3\phi/2} & 0 & 0 & 0 \\ 0 & e^{i\phi/2} & 0 & 0 \\ 0 & 0 & e^{-i\phi/2} & 0 \\ 0 & 0 & 0 & e^{-i3\phi/2} \end{pmatrix}, \tag{A5}$$

$$U_\theta = \begin{pmatrix} c^3 & \sqrt{3}\,c^2 s & \sqrt{3}\,cs^2 & s^3 \\ -\sqrt{3}\,c^2 s & c(1-3s^2) & -s(1-3c^2) & \sqrt{3}\,cs^2 \\ \sqrt{3}\,cs^2 & s(1-3c^2) & c(1-3s^2) & \sqrt{3}\,c^2 s \\ -s^3 & \sqrt{3}\,cs^2 & -\sqrt{3}\,c^2 s & c^3 \end{pmatrix},$$

with $c=\cos(\theta/2)$ and $s=\sin(\theta/2)$. The basis set is

$$|v_1) = \begin{pmatrix}1\\0\\0\\0\end{pmatrix},\quad |v_2) = \begin{pmatrix}0\\1\\0\\0\end{pmatrix},\quad |v_3) = \begin{pmatrix}0\\0\\1\\0\end{pmatrix},\quad |v_4) = \begin{pmatrix}0\\0\\0\\1\end{pmatrix}, \tag{A6}$$

where hh basis states for $\vec{\mathrm{k}}=k\hat{z}$ are $|v_1)$ and $|v_4)$ while $|v_2)$ and $|v_3)$ are the corresponding lh states. At other $\vec{\mathrm{k}}$, the lh basis states are given by Eq. (4) with $j=2,3$.

The wave function is given to first order in k by Eq. (5). This can be written as

$$|v_j\vec{\mathrm{k}}) = B(\vec{\mathrm{k}})\,|v_j\hat{k}), \tag{A7}$$

with

$$B(\vec{\mathrm{k}}) = 1 + \sum_\beta \frac{|\beta)(\beta|\hbar\vec{\mathrm{k}}\cdot\vec{\mathrm{p}}/m}{-\epsilon_\beta} .$$

The sum over lh can now be written as

$$\sum_{j=2,3} |v_j\vec{\mathrm{k}})(v_j\vec{\mathrm{k}}| = B(\vec{\mathrm{k}})\Big(\sum_{j=2,3} |v_j\hat{k})(v_j\hat{k}|\Big)B^\dagger(\vec{\mathrm{k}}). \tag{A8}$$

But

$$\sum_{j=2,3} |v_j\hat{k})(v_j\hat{k}| = \sum_{j=2,3;\,i,k=1,2,3,4} |v_i)(U_{-\phi}U_{-\theta})_{ij}(U_\theta U_\phi)_{jk}(v_k| . \tag{A9}$$

The product of the rotation operators can be simplified in the following way:

$$U_{-\phi}U_{-\theta}\begin{pmatrix}0&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&0\end{pmatrix}U_\theta U_\phi = \frac{1}{k^2}\begin{pmatrix} \frac{3}{2}k_-k_+ & -(\frac{3}{2})^{1/2}k_-k_z & \frac{-\sqrt{3}}{2}k_-^2 & 0 \\ -(\frac{3}{2})^{1/2}k_+k_z & k_z^2+\frac{1}{2}k_-k_+ & 0 & \frac{-\sqrt{3}}{2}k_-^2 \\ \frac{-\sqrt{3}}{2}k_+^2 & 0 & k_z^2+\frac{1}{2}k_-k_+ & (\frac{3}{2})^{1/2}k_-k_z \\ 0 & \frac{-\sqrt{3}}{2}k_+^2 & (\frac{3}{2})^{1/2}k_+k_z & \frac{3}{2}k_-k_+ \end{pmatrix} = AA^\dagger, \tag{A10}$$

where

$$A=\frac{1}{k}\begin{bmatrix} 0 & (\frac{3}{2})^{1/2}k_- & 0 & 0 \\ 0 & -k_z & -k_-/\sqrt{2} & 0 \\ 0 & -k_+/\sqrt{2} & k_z & 0 \\ 0 & 0 & (\frac{3}{2})^{1/2}k_+ & 0 \end{bmatrix} \tag{A11}$$

and $k_\pm=(k_x \pm ik_y)/\sqrt{2}$.

The operator A defines new basis states for the lh band

$$|\bar{v}_j\hat{k}) = \sum_i |v_i)A_{ij} \quad \text{for } j=2,3. \tag{A12}$$

These states give the same sum over lh states and yet are simpler to work with. A has a simpler form than $U_{-\phi}$ or $U_{-\theta}$ and some of the elements in A vanish. Moreover, the elements of A are written in terms of $k_\pm$ and k_z. When Eq. (A2) is integrated over all directions of $\vec{k}$ only terms with even powers of k_z and matching powers of k_- and k_+ will contribute. The use of Eq. (A11) makes it easier to identify those terms in Eq. (A2) that must be evaluated.

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[1] B. V. Zubov, L. A. Kulevskii, V. P. Makarov, T. M. Murina, and A. M. Prokhorov, Zh. Eksp. Teor. Fiz. Pis'ma Red. 9, 221 (1969) [JETP Lett. 9, 130 (1969)].

[2] R. G. Wenzel, G. P. Arnold, and N. R. Greiner, Appl. Opt. 12, 2245 (1973).

[3] A. F. Gibson, C. B. Hatch, P. N. D. Maggs, D. R. Tilley, and A. C. Walker, J. Phys. C 9, 3259 (1976).

[4] J. M. Doviak, A. F. Gibson, M. F. Kimmitt, and A. C. Walker, J. Phys. C 6, 593 (1973).

[5] C. C. Lee and H. Y. Fan, Phys. Rev. B 9, 3502 (1974).

[6] C. R. Pidgeon, B. S. Wherrett, A. M. Johnston, J. Dempsey, and A. Miller, Phys. Rev. Lett. 42, 1785 (1979).

[7] R. Braunstein and N. Ockman, Phys. Rev. 134, 499 (1964).

[8] N. G. Basov, A. Z. Grasyuk, I. G. Zubarev, V. A. Katulin, and O. N. Krokhin, Zh. Eksp. Teor. Fiz. 50, 551 (1966) [Sov. Phys.—JETP 23, 366 (1966)].

[9] S. B. Arifzhanov and E. L. Ivchenko, Fiz. Tverd. Tela (Leningrad) 17, 81 (1975) [Sov. Phys.—Solid State 17, 46 (1975)].

[10] A. Baldereschi and N. O. Lipari, Phys. Rev. B 8, 2697 (1973).

[11] G. D. Mahan, Phys. Rev. 170, 825 (1968).

[12] R. Loudon, Proc. R. Soc. London 80, 952 (1962).

[13] W. Fawcett, Proc. Phys. Soc. 85, 931 (1965).

[14] M. Neuberger, *Handbook of Electronic Materials* (Plenum, New York, 1971), Vol. 5.

[15] M. Rouzeyre, H. Mathieu, D. Auvergne, and J. Camassel, Solid State Commun. 7, 1219 (1969).

[16] S. H. Groves, C. R. Pidgeon, and J. Feinleib, Phys. Rev. Lett. 17, 643 (1966).

[17] P. Lawaetz, Phys. Rev. B 4, 3460 (1971).

[18] G. Dresselhaus and M. S. Dresselhaus, Phys. Rev. 160, 649 (1967).

[19] A. Baldereschi and N. O. Lipari, Phys. Rev. B 3, 439 (1971).

[20] L. V. Keldysh, Zh. Eksp. Teor. Fiz. 47, 1945 (1964) [Sov. Phys.—JETP 20, 1307 (1965)].

[21] S. S. Mitra, L. M. Narducci, R. A. Shatas, Y. E. Tsay, and A. Vaidyanathan, Appl. Opt. 14, 3038 (1975).

[22] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, N. J., 1957).