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Frequency- and wave-number-dependent dielectric function of semiconductors

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An expression for the long-wavelength frequency-dependent dielectric function $\epsilon(\omega)$ of a semiconductor is derived for a two-band model using a tight-binding approach. The resulting expression for $\epsilon(\omega)$ contains two parameters, one of which is related to the average energy gap between the valence and conduction bands, and the other, to the widths of these bands. The frequency- and wave-number-dependent dielectric function $\epsilon(\vec{q},\omega)$ is studied for frequencies below the band gap, and an approximate expression is obtained.

I. INTRODUCTION

The frequency- and wave-number-dependent dielectric function $\epsilon(\vec{q},\omega)$ describes the response of a system to an applied electric field and is an important quantity in the study of many physical properties of the system. Although accurate calculations[1,2] of $\epsilon(\vec{q},\omega)$ based on realistic band structures and wave functions yield excellent results, simpler model calculations are often very useful in showing the explicit dependence of the dielectric function on the band parameters. For example, the Penn[3] model, with one parameter E_g, which is related to an average optical gap between the valence and conduction bands in a semiconductor, has been widely used in studying the dielectric function.[4-6] The model also forms an important part of the Phillips[7] and Van Vechten[8] theory of bonding and ionicity in A^NB^{8-N} type crystals.

The Penn model makes use of an isotropic nearly-free-electron approach in calculating the dielectric constant. In this paper, we use a different approach based on a simple tight-binding model to evaluate the dielectric function. We obtain an expression for the long-wavelength dielectric function $\epsilon(\omega)$ which provides a satisfactory description of optical dispersion over a broad energy range. The expression for $\epsilon(\omega)$ shows explicitly the dependence of the dielectric constant on the average energy gap between the valence and conduction bands, on the bandwidths, and on the atomic coordination. We also obtain an approximate expression for the low-frequency dielectric function $\epsilon(\vec{q},\omega)$.

II. EVALUATION OF $\epsilon(\omega)$

The formal expression for $\epsilon(\vec{q},\omega)$ within the random-phase approximation and ignoring local-field corrections is[9,10]

$$\epsilon(\vec{q},\omega)=1+4\pi e^2\sum_{\vec{k}}\left[A(\vec{k},\vec{q},\omega)+A(\vec{k},\vec{q},-\omega)\right], \tag{1}$$

where

$$A(\vec{k},\vec{q},\omega)=\frac{1}{\Omega q^2}\,\frac{|\langle c,\vec{k}|e^{-i\vec{q}\cdot\vec{r}}|v,\vec{k}+\vec{q}\rangle|^2}{E_{c,\vec{k}}-E_{v,\vec{k}+\vec{q}}-\hbar\omega}. \tag{2}$$

The sum over $\vec{k}$ in Eq. (1) is taken over the extended Brillouin zone. This way, there is no need for a sum over the valence (v) and conduction (c) bands in Eq. (2). The frequency ω is assumed to have a small imaginary part, and Ω is the volume of the crystal. In order to evaluate $\epsilon(\vec{q},\omega)$, we use a simple two-band Hamiltonian H which has the following form in a tight-binding (or Wannier) representation:

$$H=V_0\sum_{i\neq i'}|v,i\rangle\langle v,i'|+(V_0+V_1)\times\sum_{i\neq i'}|c,i\rangle\langle c,i'|+E_g\sum_i|c,i\rangle\langle c,i|. \tag{3}$$

We will consider only nearest-neighbor interactions between the Wannier functions centered at the atomic sites i and i'. This Hamiltonian is suitable for an elemental semiconductor; for a z-fold atomically-coordinated system, it describes a valence band of width $|2zV_0|$, a conduction band of width $|2z(V_0+V_1)|$, and an average gap E_g between the two bands. It should be noted that in this representation there are no matrix elements of the Hamiltonian between valence and conduction states.

To transform Eqs. (1) and (2) into the tight-binding representation, we first express $A(\vec{k},\vec{q},\omega)$ in the form[11]

$$A(\vec{k},\vec{q},\omega)=\frac{1}{\Omega q^2}\int_0^\infty d\lambda\, e^{\lambda\hbar\omega}\langle c,\vec{k}|e^{-\lambda H}e^{-i\vec{q}\cdot\vec{r}}e^{\lambda H}\times|v,\vec{k}+\vec{q}\rangle\langle v,\vec{k}+\vec{q}|e^{i\vec{q}\cdot\vec{r}}|c,\vec{k}\rangle. \tag{4}$$

Equation (4) is valid below the absorption edge and must otherwise be analytically continued. Defining $B(\vec{q}, \omega) = \sum_{\vec{k}} A(\vec{k}, \vec{q}, \omega)$, we can express B in the tight-binding representation as

$$B(\vec{q}, \omega) = \frac{1}{\Omega q^2} \sum_{i,j} \int_0^\infty d\lambda \, e^{\lambda \hbar \omega} \langle c, i | e^{-\lambda H} e^{-i \vec{q} \cdot \vec{r}} e^{\lambda H} \times | v, j \rangle \langle v, j | e^{i \vec{q} \cdot \vec{r}} | c, i \rangle . \tag{5}$$

Setting $\vec{q} = q\hat{x}$, let us first consider the $q \to 0$ limit of Eq. (5) which is given by

$$B(\omega) = \frac{1}{\Omega} \sum_{i,j} \int_0^\infty d\lambda \, e^{\lambda \hbar \omega} \langle c, i | e^{-\lambda H} x e^{\lambda H} \times | v, j \rangle \langle v, j | x | c, i \rangle . \tag{6}$$

To evaluate $B(\omega)$, we will start by making a simple approximation which will prove very useful. We will assume that the only nonzero matrix elements of x are between two sites on the same orbital, i.e.,

$$| \langle v, i | x | c, j \rangle |^2 = | x_{vc} |^2 \delta_{ij} . \tag{7}$$

Without using this approximation, the same results can be obtained if, in Eq. (2), we replace the $\vec{k}$-dependent matrix elements (in the limit $\vec{q} \to 0$) by an "average" matrix element $| x_{vc} |^2$. For a simple model of nondegenerate valence and conduction bands, the matrix element $| x_{vc} |^2$ defined by Eq. (7) will, in general, be zero except for crystals of low symmetry. For the moment, let us assume that we have degenerate and noninteracting valence bands of different symmetries so that $| x_{vc} |$ is different from zero. Making use of this "site approximation" we find

$$B(\omega) = n \int_0^\infty d\lambda \, e^{\lambda \hbar \omega} \langle c, 0 | e^{-\lambda H} x e^{\lambda H} | v, 0 \rangle x_{vc} , \tag{8}$$

where n is the number of electrons per unit volume. Expanding the exponentials and integrating over λ, we obtain

$$B(\omega) = \left(\frac{1}{E_g - \hbar \omega} \right) \left[1 + \sum_{m=2}^{\infty} \left(\frac{V_1}{E_g - \hbar \omega} \right)^m N_m \right] n | x_{vc} |^2 , \tag{9}$$

where N_m is the total number of paths which starting at a given site, return to the same site after m-displacements (each displacement being from a site to one of its nearest neighbors). Thus N_m depends only on the topology of the structure under consideration. The long-wavelength frequency-dependent dielectric function $\epsilon(\omega) = \epsilon(\vec{q} = 0, \omega)$ is given by $\epsilon(\omega) = 1 + 4\pi e^2 [B(\omega) + B(-\omega)]$.

The function $B(\omega)$ has several interesting features. First, the terms in the infinite sum in Eq. (9) give the corrections to a single-gap model of $\epsilon(\omega)$. Second, $B(\omega)$ depends on V_1 but not on V_0. This is not very surprising if we note that when $V_1 = 0$, the valence and conduction bands have the same curvature everywhere, and there is a constant energy gap E_g between the two bands. For this case, Eq. (9) is seen to give the one gap result. Depending on the signs of V_0 and $V_0 + V_1$, V_1 is related either to the sum or the difference of the bandwidths of the valence and conduction bands. When the valence and conduction bands have opposite curvatures, V_1 is related to the sum of the bandwidths.

Before proceeding with an evaluation of $B(\omega)$ for special cases, we would like to discuss how the inclusion of other matrix elements affects $B(\omega)$. It can be shown that when we go beyond the site approximation, we obtain (i) a term with the same frequency dependence as $B(\omega)$, and (ii) correction terms which for frequencies much smaller than the band gap are proportional to $[V_1/(E_g - \hbar\omega)]^n \times B(\omega)$ with $n \geq 1$. The proportionality constant is related to the matrix element of orbitals on atoms n nearest neighbors away from one another and is expected to decrease rapidly in magnitude as n becomes large. If $V_1/E_g \ll 1$ (as we show below, it is about 0.15 in Si), then the effects of these extra terms for low frequencies can be absorbed into the matrix element $| x_{vc} |^2$, and the use of the site approximation results in a fractional error of the order of $(V_1/E_g)(\hbar\omega/E_g)(1 + \hbar\omega/E_g)$ in $B(\omega)$. Since $\epsilon(\omega)$ is related to the sum $B(\omega) + B(-\omega)$, the fractional error in $\epsilon(\omega)$ for small frequencies will be of the order of $(V_1/E_g)(\hbar\omega/E_g)^2$, which is extremely small in general. For higher frequencies in the region where absorption occurs, higher-order matrix elements of H and x need to be considered to obtain accurate results.

The explicit evaluation of $B(\omega)$ as given by Eq. (7) is, in general, very difficult. This equation, as it stands, is not very useful since it involves an infinite sum and one must be concerned with questions of convergence, particularly when $\hbar\omega$ is near the energy gap E_g. The sum can be expressed as a matrix element of the Green's function for a simple one-band Hamiltonian. We think it is instructive to consider a case where the sum can be evaluated explicitly for all frequencies. The Bethe lattice[12] provides such a case, and as we show below, it introduces a negligible error for frequencies below the gap when $V_1/E_g \ll 1$. For a z-fold-coordinated Bethe lattice, defining

$$B_{\pm}(\omega) = \frac{2(z-1) n | x_{vc} |^2}{(z-2)(E_g - \hbar\omega) \pm z [(E_g - \hbar\omega)^2 - 4(z-1) V_1^2]^{1/2}} , \tag{10}$$

we find

$$\epsilon(\omega) = 1 + 4\pi e^2[B_+(\omega) + B_+(-\omega)] \tag{11}$$

when

$$0 \leq \hbar\omega \leq E_g + 2(z-1)^{1/2}|V_1|,$$

and

$$\epsilon(\omega) = 1 + 4\pi e^2[B_-(\omega) + B_+(-\omega)] \tag{12}$$

when

$$\hbar\omega \geq E_g + 2(z-1)^{1/2}|V_1|.$$

For the Bethe lattice, the band gap has the value $E_g - 2(z-1)^{1/2}|V_1|$, and for frequencies ranging from the gap to $E_g + 2(z-1)^{1/2}|V_1|$, $\epsilon(\omega)$ is complex and can be expressed as $\epsilon_1(\omega) - i\epsilon_2(\omega)$. Because of the use of the site approximation, $\epsilon_2(\omega)$ is not accurately determined in our model; however, $\epsilon_1(\omega)$ is accurate when $\hbar\omega \ll E_g - 2(z-1)^{1/2}|V_1|$, and $\hbar\omega \gg E_g + 2(z-1)^{1/2}|V_1|$. Even though Eq. (11) gives only an approximate $\epsilon_2(\omega)$ spectrum, the sum rule

$$\int_0^\infty \omega\epsilon_2(\omega)d\omega = \frac{\pi}{2}\,\omega_p^2, \tag{13}$$

where ω_p is the valence electron plasma frequency, must be satisfied in order for $\epsilon_1(\omega)$ to have the correct high-frequency behavior. The plasma-sum rule yields the result

$$8\pi n e^2|x_{vc}|^2 = (\hbar\omega_p)^2/E_g \tag{14}$$

independent of the parameter V_1 or the coordination number z. The result is also independent of the use of the Bethe lattice instead of the real lattice and can be expressed as $|x_{vc}|^2 = 1/E_g$, when E_g is measured in Rydbergs and $|x_{vc}|$ in Bohr units. Our model for $\epsilon(\omega)$ therefore contains only the two independent parameters E_g and V_1. In practice the actual value of $|x_{vc}|^2$ is larger than E_g^{-1} because of core-electron contributions. The magnitude of the correction factors have been obtained by Van Vechten[8] for a number of crystals.

We have used Eq. (11) to fit the low-frequency-refractive-index data of Si and Ge in order to obtain the values of the parameters E_g and V_1. In Si, a fit of the measured[13] refractive-index data in the energy range 0.1–1.2 eV yields $E_g = 5.36$ eV and $|V_1| = 0.80$ eV. A similar fit of the data[13] for Ge in the energy range 0.1–0.6 eV gives $E_g = 4.46$ eV and $|V_1| = 0.88$ eV. The ratio V_1/E_g is very small and is about 0.15 (0.20) in Si (Ge). As a result of this, for $\omega \to 0$, the infinite sum in Eq. (9) converges very rapidly, and the use of the Bethe lattice instead of the diamond lattice results in a negligible error in the evaluation of $\epsilon_1(0)$. For Si, for example, this error is about $\frac{1}{2}\%$. The small value of V_1/E_g also ensures that the site approximation leads to only a small error in $\epsilon_1(\omega)$ for low frequencies, as we have already discussed. In Fig. 1, we show the real and imaginary parts of $\epsilon(\omega)$ for Si as determined by our model. The ϵ_1 spectrum for a one-gap model with $E_g = 5.36$ eV is also shown for comparison. It is interesting to note that our model gives a threshold for ϵ_2 at 2.6 eV as compared with the experimental value[14] of about 3.4 eV.

III. EVALUATION OF $\epsilon(\vec{q},\omega)$

To obtain the $\vec{q}$ dependence of the dielectric function, we need to evaluate the function $B(\vec{q},\omega)$ given by Eq. (5). $B(\vec{q},\omega)$ can be written more symmetrically as

$$B(\vec{q},\omega) = \frac{1}{2}\frac{n}{q^2}\sum_j\left(\int_0^\infty d\lambda\, e^{\lambda\hbar\omega}\langle c,0|e^{-\lambda H}e^{-i\vec{q}\cdot\vec{r}}e^{\lambda H}|v,j\rangle\langle v,j|e^{i\vec{q}\cdot\vec{r}}|c,0\rangle\right.$$
$$\left.+\int_0^\infty d\lambda\, e^{\lambda\hbar\omega}\langle c,0|e^{-i\vec{q}\cdot\vec{r}}|v,j\rangle\langle v,j|e^{\lambda H}e^{i\vec{q}\cdot\vec{r}}e^{-\lambda H}|c,0\rangle\right), \tag{15}$$

where n is the number of electrons per unit volume as before. In the model we are using, all atoms are assumed to be equivalent; in a more detailed treatment, the site 0 should be replaced by a sum over the position of all the atoms in the basis, and an average of the resulting expressions for $B(\vec{q},\omega)$ should be used. As in Sec. II, we now assume the only nonzero matrix elements of $\vec{r}$ to be of the type

$$\langle v,j|\vec{r}|c,i\rangle = \vec{r}_{vc}\,\delta_{ij}. \tag{16}$$

This approximation can be used to obtain

$$\langle v,j|e^{i\vec{q}\cdot\vec{r}}|c,m\rangle = ie^{i\vec{q}\cdot\vec{R}_j}\sin\vec{q}\cdot\vec{r}_{vc}\,\delta_{jm}, \tag{17}$$

where $\vec{R}_j$ is the position vector of the jth atom with respect to the atom at the origin and labeled by 0 in Eq. (5). Inserting a complete set of states between the various exponentials in the expression for $B(\vec{q},\omega)$ and using Eq. (17), we find

$$B(\vec{q},\omega) = \frac{n\sin^2\vec{q}\cdot\vec{r}_{vc}}{q^2}\sum_j\int_0^\infty d\lambda\, e^{\lambda\hbar\omega}\langle c,0|$$
$$\times e^{-\lambda H}|c,j\rangle\langle v,j|e^{\lambda H}|v,0\rangle\cos\vec{q}\cdot\vec{R}_j. \tag{18}$$

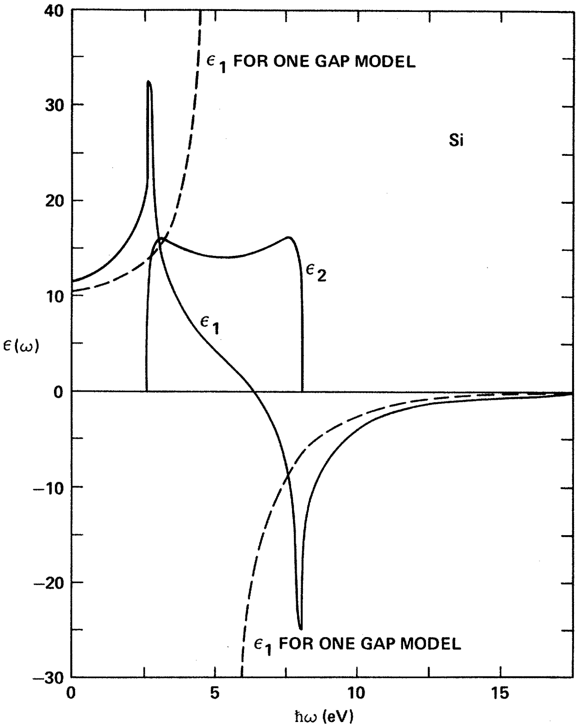

FIG. 1. Real (ϵ_1) and imaginary (ϵ_2) parts of the frequency-dependent dielectric function for a fourfold coordinated Bethe lattice with interaction parameters fitted to the low-frequency dispersion data in Si. ϵ_1 spectrum for a one-gap model is also shown.

The function $B(\vec{q}, \omega)$ has a number of interesting properties. For example, as we will show below the largest contribution to $B(\vec{q}, \omega)$, in the low-frequency region, comes from the $j = 0$ term of the sum in Eq. (18). This immediately implies that for small frequencies (i.e., $\hbar\omega \ll$ band gap) the $\vec{q}$ dependence of the dielectric function goes as

$$h(\vec{q}) = \sin^2 \vec{q} \cdot \vec{r}_{vc} / q^2 \tag{19}$$

and

$$\epsilon(\vec{q}, \omega) - 1 \simeq f(\vec{q})[\epsilon(\omega) - 1], \tag{20}$$

where $f(\vec{q})$ is proportional to $h(\vec{q})$.

Let us now consider the application of Eq. (18) to cubic crystals. It is clear that $h(\vec{q})$, given by Eq. (19), does not have the symmetry properties required to describe $\epsilon(\vec{q})$ in these crystals. For example, the $|\vec{q}| \to 0$ limit of Eq. (19) depends on the direction of $\vec{q}$, and this is incompatible with the behavior of $\epsilon(\vec{q})$ in cubic crystals. The problem arises from using a set of singly degenerate valence and conduction bands with a nonzero matrix element $\vec{r}_{vc}$ between them. As already mentioned in Sec. II, $\vec{r}_{vc}$ is nonzero if we assume that we have degenerate valence (or conduction) bands of different symmetry. When these degenerate bands arise from basis sets with s, p_x, p_y, and p_z symmetry, the expression for $h(\vec{q})$ is given by

$$h(\vec{q}) = (\sin^2 q_1 x_{vc} + \sin^2 q_2 y_{vc} + \sin^2 q_3 z_{vc}) / q^2 , \tag{21}$$

with $|x_{vc}| = |y_{vc}| = |z_{vc}|$, and for low frequencies,

$$\epsilon(\vec{q}, \omega) - 1 \simeq [h(\vec{q}) / |q x_{vc}|^2][\epsilon(\omega) - 1]. \tag{22}$$

The effect of including other matrix elements such as x_{vv} (defined in a similar way to x_{vc}), leads to the same $\vec{q}$ dependence as that given by Eqs. (21) and (22), but with x_{vc} replaced by

$$x_{vc} \to [(x_{vc})^2 + (x_{vv}/2)^2]^{1/2}. \tag{23}$$

For Si, we have used an effective $|x_{vc}|$ equal to $2.2\, a/2\pi$, where a is the cubic lattice constant to evaluate $\epsilon(\vec{q})$ in the [100] direction. The result is shown in Fig. 2 (dash-dot-dash line) and compared to the results of Walter and Cohen[1] and Srinivasan.[4] The calculations of Walter and Cohen[1] involve the detailed band structure and wave functions of Si, and Srinivasan's calculation[4] is based on the free-electron model of Penn.[3] The finite slope of $\epsilon(\vec{q})$ at $\vec{q} = 0$ and the maximum in $\epsilon(\vec{q})$ for small $|\vec{q}|$ in Srinivasan's calculation are probably caused by the approximations used in evaluating the dipole matrix elements. Figure 2 shows that compared to the results of Ref. 1, Eq. (22) overestimates $\epsilon(\vec{q})$ for small $|\vec{q}|$. To improve the accuracy of $\epsilon(\vec{q})$, we need to include higher-order interactions and dipole matrix elements in our derivation. The inclusion of higher excited states and matrix elements has the effect of making $\epsilon(\vec{q})$ more

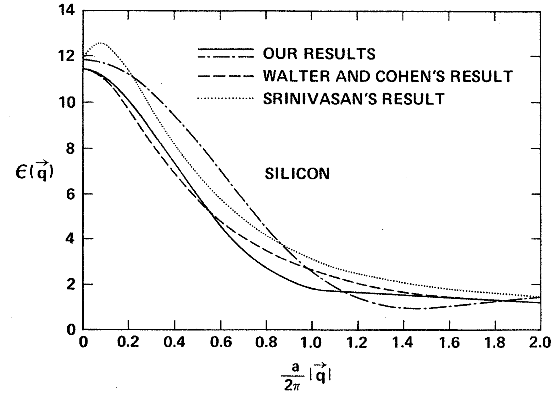

FIG. 2. Wave-vector-dependent dielectric constant $\epsilon(\vec{q}, 0)$ for $\vec{q}$ along the [100] direction obtained from our model calculations (solid line, and dash-dot-dash line) as compared to the results of Walter and Cohen (Ref. 1, dashed line) and Srinivasan (Ref. 4, dotted line).

isotropic because of the increase in the number of directions for $\vec{r}_{vc}$. It is interesting, therefore, to examine the $\vec{q}$ dependence of a completely symmetrized $h(\vec{q})$ when an average over all possible directions of $\vec{r}_{vc}$ is taken in Eq. (19) (assuming $|\vec{r}_{vc}|$ is constant). This average is given by

$$h(\vec{q}) = (1/2q^2)[1 - (\sin 2qr_{vc}/2qr_{vc})] , \tag{24}$$

where $r_{vc} = |\vec{r}_{vc}|$. The low-frequency dielectric function is equal to

$$\epsilon(\vec{q}, \omega) \simeq 1 + [3/2(qr_{vc})^2][1 - (\sin 2qr_{vc}/2qr_{vc})] [\epsilon(\omega) - 1]. \tag{25}$$

For Si we have used an effective r_{vc} equal to $2.2(3)^{1/2}a/2\pi$ to evaluate $\epsilon(\vec{q}, 0)$ using Eq. (25). The result for $\vec{q}$ along the [100] direction is also shown in Fig. 2 (solid line). To facilitate comparison with the results of Ref. 1, we have fitted $\epsilon(0)$ to their calculated value of 11.2. Equation (25) is seen to provide a much better agreement with the results of the detailed calculation[1] than Eq. (22). The isotropy of $\epsilon(\vec{q})$ suggested by Eq. (25) is also in good agreement with the results of calculations[1] which show that the anisotropy in $\epsilon(\vec{q})$ is very small.

The factorization of $\epsilon(\vec{q}, \omega)$ into $f(\vec{q})[\epsilon(\omega) - 1]$ resulted from the assumption that the most important term in Eq. (18) was the $j = 0$ term. We will now compare the various terms in the expansion and show that this assumption is justified. For frequencies below the band gap, the leading term for $j = 0$ is of the form $1/(E_g - \hbar\omega)$. The next important term occurs when j is a nearest neighbor of the site labeled 0 and is of the form $[- V_0(V_0 + V_1)/(E_g - \hbar\omega)^3]\cos\vec{q}\cdot\tau$, where $\vec{\tau}$ is the position vector of the nearest-neighbor atom. Let us assume that the valence and conduction bands have opposite curvatures at $\vec{k} = 0$, so that V_0 and $(V_0 + V_1)$ have different signs. The value of $|V_1|$ is not arbitrary but can be determined from fitting the optical dispersion data as we have done for Si and Ge in Sec. II. The maximum value (in magnitude) of the product $V_0(V_0 + V_1)$ occurs when $(V_0 + V_1) = \frac{1}{2} V_1$ and $V_0 = -\frac{1}{2} V_1$. The terms corresponding to the nearest-neighbor j's are therefore smaller by a factor of $\frac{1}{4} V_1^2(E_g - \hbar\omega)^{-2}$ than the intra-atomic term. Since in Si (Ge) the ratio $|V_1|/E_g$ is about 0.15 (0.20), neglect of interatomic terms results in a small error (of about 5%) in the evaluation of $\epsilon(\vec{q}, \omega)$ for low frequencies.

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[1] J. P. Walter and M. L. Cohen, Phys. Rev. B 2, 1821 (1970).

[2] J. P. Walter and M. L. Cohen, Phys. Rev. B 5, 3101 (1972); S. J. Sramek and M. L. Cohen, *ibid.* 6, 3800 (1972).

[3] D. R. Penn, Phys. Rev. 128, 2093 (1962).

[4] G. Srinivasan, Phys. Rev. 178, 1244 (1969).

[5] W. Brandt and J. Reinheimer, Can. J. Phys. 46, 607 (1968); Phys. Rev. B 2, 3104 (1970).

[6] R. A. Breckenridge, R. W. Shaw, Jr., and A. Sher, Phys. Rev. B 10, 2483 (1974).

[7] J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970).

[8] J. A. Van Vechten, Phys. Rev. 182, 891 (1969).

[9] P. Nozières and D. Pines, Phys. Rev. 109, 762 (1958).

[10] H. Ehrenreich and M. H. Cohen, Phys. Rev. 115, 786 (1959).

[11] Use of an integral representation has been previously considered by R. M. White in calculations on the magnetic susceptibility. See Phys. Rev. B 10, 3426 (1974).

[12] Bethe lattice is a mathematical construct in which the nearest-neighbor coordination of each atom is satisfied but no closed loops or rings of atoms are permitted. For more details see, for example, the article by M. F. Thorpe and D. Weaire in Phys. Rev. B 10, 3518 (1971).

[13] C. D. Salzberg and J. J. Villa, J. Opt. Soc. Am. 47, 244 (1957).

[14] R. L. Zucca and Y. R. Shen, Phys. Rev. B 1, 2668 (1970).