[5] L. Liu and E. Tosatti, Phys. Rev. Letters 23, 772 (1969).

[6] J. G. Broerman, Phys. Rev. Letters 24, 450 (1970).

[7] J. G. Broerman, Phys. Rev. B 1, 4568 (1970).

[8] E. D. Hinkley and A. W. Ewald, Phys. Rev. 134, A1260 (1964).

[9] O. N. Tufte and A. W. Ewald, Phys. Rev. 122, 1413 (1961).

[10] J. G. Broerman, Phys. Rev. 183, 754 (1969).

[11] C. R. Whitsett, Phys. Rev. 138, A829 (1965).

[12] R. R. Galazka, D. G. Seiler, and W. M. Becker, Phys. Rev. (to be published). I am much indebted to these authors for communication of their work to me prior to publication.

[13] S. L. Lehoczky and D. A. Nelson (private communication).

[14] C. R. Whitsett, S. L. Lehoczky, and J. G. Broerman, Bull. Am. Phys. Soc. 15, 315 (1970).

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

[16] Private communications from R. R. Galazka, C. R. Whitsett, S. L. Lehoczky, and D. A. Nelson.

[17] V. I. Ivanov-Omskii, B. T. Kolomietz, V. K. Ogorodnikov, and K. P. Smekalova, Fiz. Tekh. Poluprov. 4, 264 (1970) [Soviet Phys. Semicond. 4, 214 (1970)].

[18] C. R. Pidgeon and S. H. Groves, in *II – VI Semiconducting Compounds*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 1080.

[19] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).

[20] D. H. Dickey and J. G. Mavroides, Solid State Commun. 2, 213 (1964).

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Wave-Vector-Dependent Dielectric Function for Si, Ge, GaAs, and ZnSe[†]

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The longitudinal wave-vector-dependent dielectric function $\epsilon(\vec{q})$ is calculated for Si, Ge, GaAs, and ZnSe. The energy eigenvalues and wave functions which are used have been obtained from energy-band calculations based on the empirical pseudopotential method. Explicit results are given in the [1,0,0], [1,1,0], and [1,1,1] directions in the range $0 \le q \le (4\pi/a)$. A comparison is made between the present results and the results of other calculations. Some comparisons with experiment are also made.

I. INTRODUCTION

In this paper we present a calculation of the static longitudinal wave-vector-dependent dielectric function $\epsilon(\vec{q})$ for the cubic semiconductors Si, Ge, GaAs, and ZnSe. $\epsilon(\vec{q})$ describes the response of a crystal to an electric field parallel to $\vec{q}$:

$$\vec{D}e^{i\vec{q}\cdot\vec{r}} = \epsilon(\vec{q})\vec{E}e^{i\vec{q}\cdot\vec{r}} \quad . \tag{1.1}$$

For most applications we are interested in either static fields or fields varying with phonon frequencies; in this frequency region we may replace the frequency-dependent dielectric function with the static dielectric function $\epsilon(\vec{q})$, an approximation which is accurate to within 0.1%.

Using the expression for $\epsilon(\vec{q})$ given by Ehrenreich and Cohen,[1] we obtain

$$\epsilon(\vec{q}) = 1 + \frac{8\pi e^2}{q^2} \sum_{\vec{k},c,v} \frac{|\langle \vec{k}+\vec{q}, v | \vec{k}, c\rangle|^2}{E_c(\vec{k}) - E_v(\vec{k}+\vec{q})} \quad , \tag{1.2}$$

where $\vec{k}$ is summed over the first Brillouin zone, v over the valence bands, and c over the conduction bands. In our calculations we use electronic wave functions and energy eigenvalues which have been calculated using the empirical pseudopotential method.[2] Spin-orbit effects have not been included.

Calculations of $\epsilon(\vec{q})$ for semiconductors were first performed by Penn,[3] using a model isotropic semiconductor. These calculations have recently been redone by Srinivasan.[4] The present calculations agree fairly well with Srinivasan's calculations except that our results exhibit a slight anisotropy. Calculations based on more realistic band models for Si and Ge have been performed by Nara.[5] Despite the fact that his model is almost identical to ours, his results disagree to some extent with our results. In particular, he finds a strong anisotropy in $\epsilon(\vec{q})$ at small q which is missing from our results. In addition, our calculations show $\epsilon(\vec{q})$ to be a monotonically decreasing function of $|\vec{q}|$, a feature which is not present in the results of Srinivasan or of Nara (see Fig. 1).

$\epsilon(\vec{q})$ has had many applications; it has been used to calculate the lattice vibration spectrum of sili-

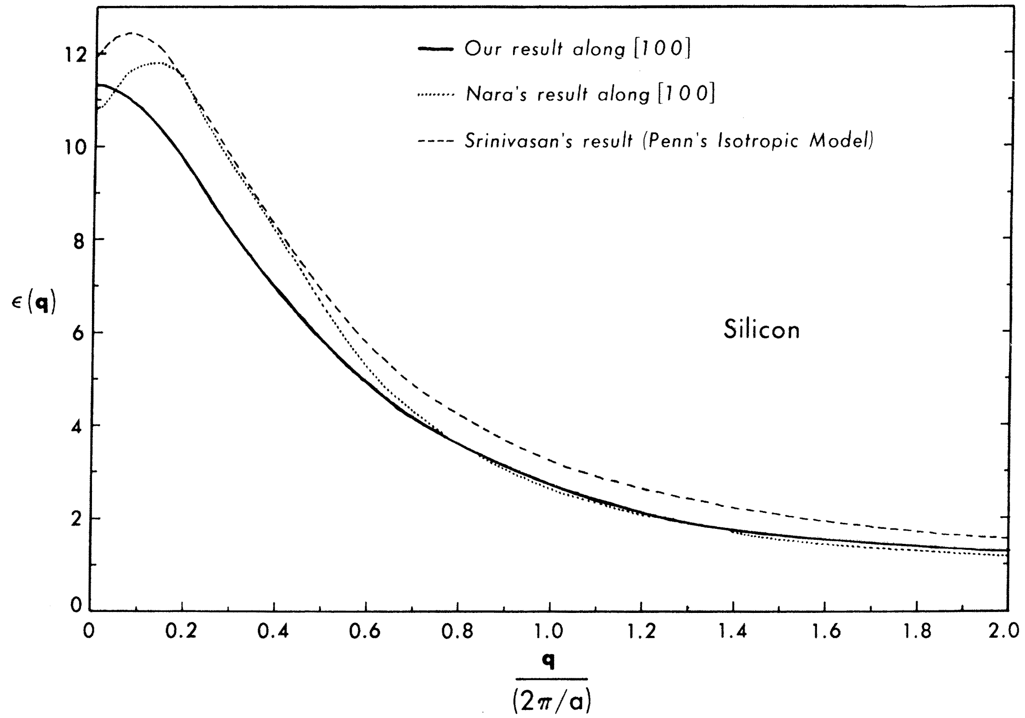

FIG. 1. Our calculation of the microscopic longitudinal dielectric function of silicon compared with the calculations by Srinivasan (Ref. 4) and by Nara (Ref. 5).

con,[6] screened pseudopotential form factors,[7] and screened impurity potentials.[8]

II. CALCULATIONS

For the purposes of calculation Eq. (1.1) is written as follows:

$$\epsilon(\vec{q}) = 1 + \frac{8\pi e^2}{q^2}\,\frac{2}{(2\pi)^3} \times \sum_{\Delta k, c, v} \frac{|\langle \vec{k}+\vec{q}, v \,|\, \vec{k}, c\rangle|^2 (\Delta k)^3}{E_c(\vec{k}) - E_v(\vec{k}+\vec{q})}\,, \qquad (2.1)$$

where the summation is over cubes of volume $(\Delta k)^3$ in the first Brillouin zone, with suitable truncations at the zone boundaries. The summation index v spans the top four valence bands, and the index c spans the bottom 11 conduction bands. For the semiconductors we consider, $E_c(\vec{k})$ is always greater than $E_v(\vec{k}+\vec{q})$, and thus each contribution to $\epsilon(\vec{q})$ is positive.

The energy eigenvalues and eigenvectors are calculated using the empirical pseudopotential method, as described in Ref. 2. The pseudopotential form factors (Table I) have been adjusted so that the reflectivity and the principal optical gaps agree with experimental measurements.[9] Fifteen energy eigenvalues and eigenvectors are computed for each of 3360 points in the first Brillouin zone. The coordinates of the grid of calculated points are given by $\frac{1}{16}(2s+1,\ 2m+1,\ 2n+1)$ in units of $2\pi/a$, where s, m, and n are integers.

For an arbitrary direction of $\vec{q}$, the summation in Eq. (2.1) must be performed over the entire Brillouin zone. Fortunately, symmetry properties can be exploited to reduce the computation time by a factor of 8 in the [100] direction, by 6 in the [111] direction, and by 4 in the [110] direction. The computation time for a particular value of $\vec{q}$ can be reduced by an additional factor of 15 if $\vec{q}$ is chosen such that $(\vec{k}+\vec{q})$ also lies on the grid of cal-

TABLE I. Lattice constants and pseudopotential form factors (in Ry) used in our calculations.

	Lattice const (Å)	$V^S(3)$	$V^S(8)$	$V^S(11)$	$V^A(3)$	$V^A(4)$	$V^A(11)$
Si	5.43	−0.21	0.04	0.08	0	0	0
Ge	5.66	−0.23	0.01	0.06	0	0	0
GaAs	5.64	−0.246	−0.001	0.074	0.058	0.051	0.001
ZnSe	5.65	−0.213	−0.011	0.067	0.203	0.107	0.015

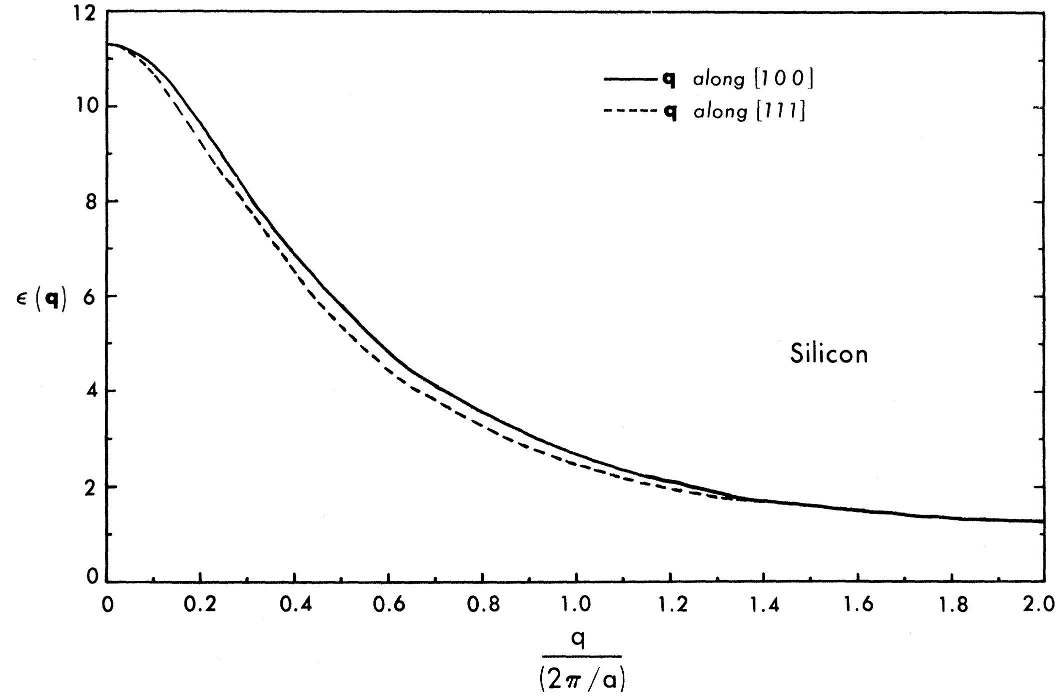

FIG. 2. Calculated microscopic dielectric function of Si along two symmetry directions. $\epsilon(\vec{q})$ for $\vec{q}$ along [110] is essentially the same as for $\vec{q}$ along [100].

culated points.

The 3360 points in the summation over the Brillouin zone provide sufficiently accurate convergence. Other calculations[10] of $\epsilon(0)$ using over 3 000 000 points in the Brillouin zone differ from our values of $\epsilon(0)$ by less than 3%.

III. RESULTS

The calculated dielectric functions of Si, Ge, GaAs, and ZnSe appear in Figs. 2–5. For all four crystals, $\epsilon(\vec{q})$ is a smooth monotonically decreasing function of $|\vec{q}|$, with zero gradient at $\vec{q}=0$. The value of $\epsilon(\vec{q})$ was calculated at several points for small $\vec{q}$ to make certain it exhibited no maximum (for $\vec{q}\neq 0$). Such maxima do occur in the results of Srinivasan[4] and of Nara.[5]

$\epsilon(\vec{q})$ in the [110] direction is practically indistinguishable from $\epsilon(\vec{q})$ in the [100] direction. The values of $\epsilon(\vec{q})$ in the [111] direction are slightly less than in the other directions. A possible reason for this slight anisotropy is that the [111] direction is the direction to the nearest-neighboring atoms in the crystal. Between nearest neighbors there is good evidence for localized bonding charges. This has been confirmed by x-ray diffraction experiments for diamond.[11] This localized electronic charge constrains the electronic charge distribution and seems to prevent the screening from being as effective. Consequently, $\epsilon(\vec{q})$ is lower in magnitude in the [111] direction than in the other directions.

IV. COMPARISON

As stated above, our calculations show that $\epsilon(\vec{q})$ decreases as $|\vec{q}|$ increases, and there exists little anisotropy for small q. This decrease in $\epsilon(\vec{q})$ is in contrast to the results of Srinivasan,[4] who finds that $\epsilon(\vec{q})$ increases in this region. However, he does note that this increase is sensitive to his choice of matrix elements.

Our results for small q also contrast with the results of Nara.[5] Nara finds that $\epsilon(\vec{q})$ increases rapidly and is remarkably anisotropic for small q. From our experience with these calculations, we find that great care must be taken when we calculate the inner products for small q. The inner product of the two Bloch wave functions $u_n(\vec{k})$ and $u_m(\vec{k}+\vec{q})$ should go smoothly to zero as $\vec{q}\to 0$, but for certain points k in the zone there occur discontinuities in the inner products as $\vec{q}\to 0$. The reason for such a discontinuity is that in the pseudopotential method the wave functions $u_n(\vec{k})$ and $u_m(\vec{k}+\vec{q})$ are expanded in two different sets of plane waves, the first set satisfying the criterion $|\vec{k}+\vec{G}|^2 \leq 7$, and the second set satisfying $|\vec{k}+\vec{q}+\vec{G}|^2 \leq 7$. The immediate effect is to cause the absolute values of these inner products to increase much too rapidly. The over-all effect does produce sizable errors in $\epsilon(\vec{q})$, especially for small q, and in particular, it produces a humplike effect similar to the results of Nara at small q. When we use the proper approach of expanding the wave function $u_m(\vec{k}+\vec{q})$ in the same set of plane waves as for $u_n(\vec{k})$, we obtain no maxima for nonzero q and little anisotropy for small q. It should be noted that for larger q, good agreement exists between our results and the results of Nara.

In Fig. 1 we compare our calculation of the dielectric function of silicon with the calculations by Srinivasan and by Nara. We obtain a value for $\epsilon(0)$ of 11.3 for Si, while Nara obtains a value of 10.8. The measured value is 11.7 ± 0.2,[12] a value which Srinivasan uses as a parameter in his model. For Ge, GaAs, and ZnSe we obtain values for $\epsilon(0)$ of 14.0, 8.9, and 4.8, respectively, while the measured values are 15.8 for Ge,[12] 10.9 for GaAs,[13] and 5.9 for ZnSe.[14]

V. APPLICATIONS

An immediate application of our results is a more precise calculation of screened pseudopotential form factors, as suggested by Phillips[7] and by Srinivasan.[4] In particular, our calculations allow us to evaluate the pseudopotential form factor $V_p(G_1)$ for Si. [G_1 is the magnitude of the first reciprocal-lattice vector $2\pi/a(111)$.] Now the screened pseudopotential form factors for Si have already been calculated by Animalu and Heine,[15] but they used the Hartree free-electron dielectric function[16] $\epsilon_f(\vec{q})$ to screen the ion core instead of the correct dielectric function $\epsilon(\vec{q})$. We propose to demonstrate that by using our $\epsilon(\vec{q})$ as the screening function, we obtain a value of $V_p(G_1)$ for Si remarkably close to the empirically determined value,[9] *provided that we include an exchange correction term.*

Animalu and Heine screened the atomic form factor $V_a(q)$ for Si with the function $X_f(q)$:

$$V_p(\vec{q}) = V_a(\vec{q})/X_f(\vec{q}),$$

where

$$X_f(\vec{q}) = 1 + [\epsilon_f(\vec{q}) - 1][1 - \tfrac{1}{2}q^2(q^2 + k_s^2 + k_F^2)^{-1}] .$$

The quantity in the second bracket is an approximation suggested by Hubbard[17] to account for the exchange correction on a free-electron gas. (Animalu and Heine chose $k_s = 2k_F/\pi$.) For $\vec{q} = \vec{G}_1$, the value of this exchange term is 0.77. For a free-electron gas with the density of the valence electrons of Si, $\epsilon_f(G_1) = 1.98$, so that $X_f(G_1) = 1.76$. If the correct $X(q)$ is defined in an analogous manner to $X_f(q)$, with $\epsilon(q)$ replacing $\epsilon_f(q)$, our value of $\epsilon(G_1) = 1.43$ gives $X(G_1) = 1.33$.

The complete pseudopotential $V_p(G_1)$ must also account for the bonding charges. Since $\epsilon(0) = 11.7$ for Si, there is a charge of $2e/\epsilon(0)$ in each of the bonding charges located midway between nearest Si atoms. The total expression is

$$V_p(q) = V_a(q) + [S_b(q)/S_a(q)]\, V_b(q) ,$$

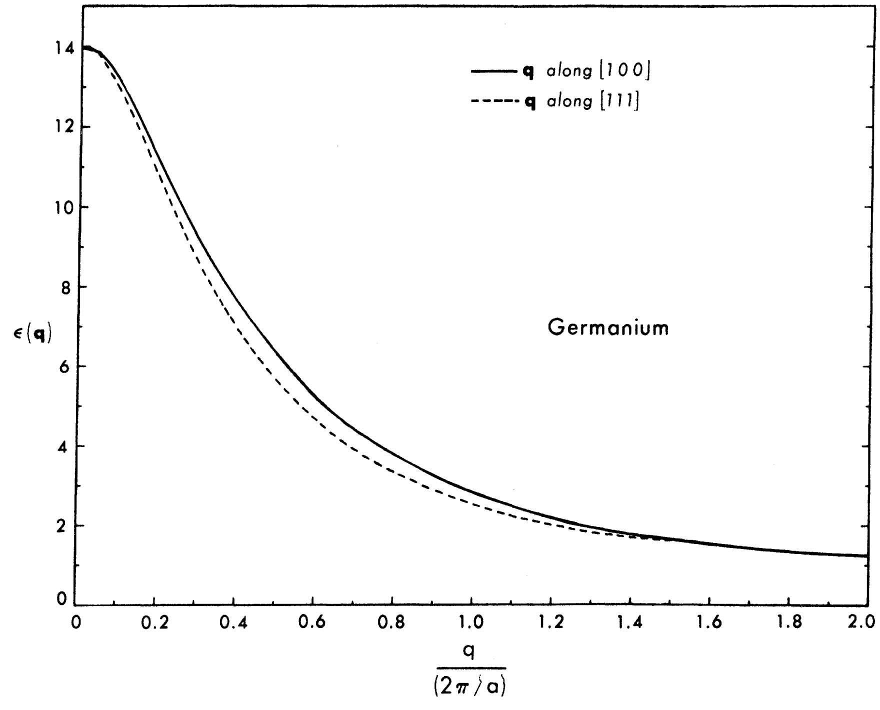

FIG. 3. Calculated microscopic dielectric function of Ge along two symmetry directions. $\epsilon(\vec{q})$ for $\vec{q}$ along [110] is essentially the same as for $\vec{q}$ along [100].

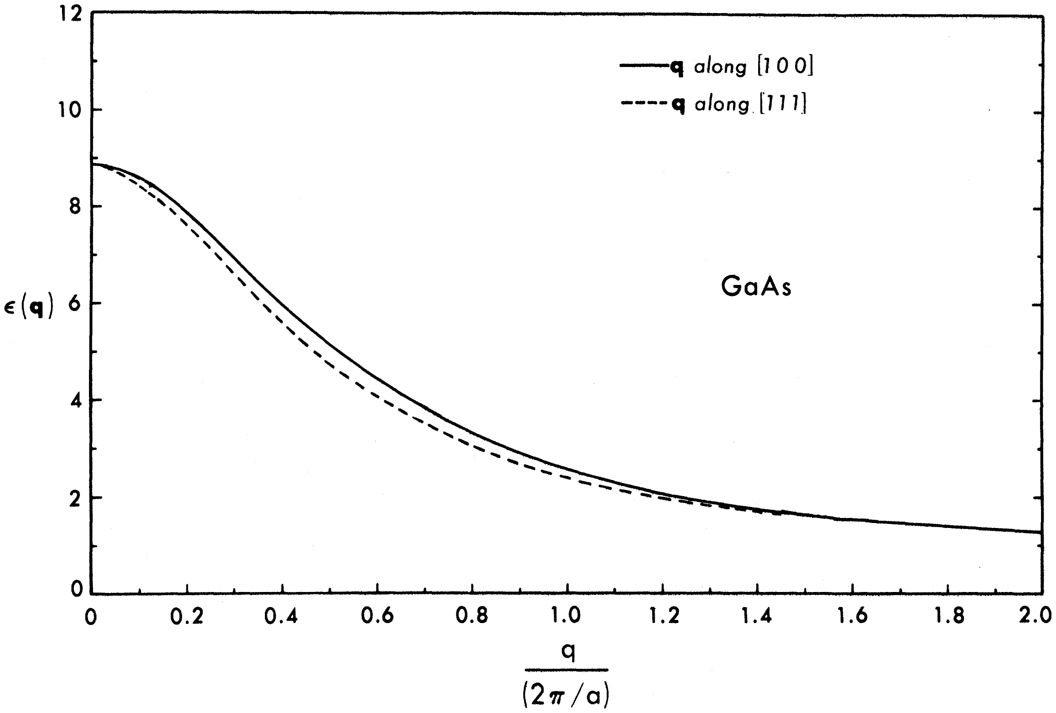

FIG. 4. Calculated microscopic dielectric function of GaAs along two symmetry directions. $\epsilon(\vec{q})$ for $\vec{q}$ along [110] is essentially the same as for $\vec{q}$ along [100].

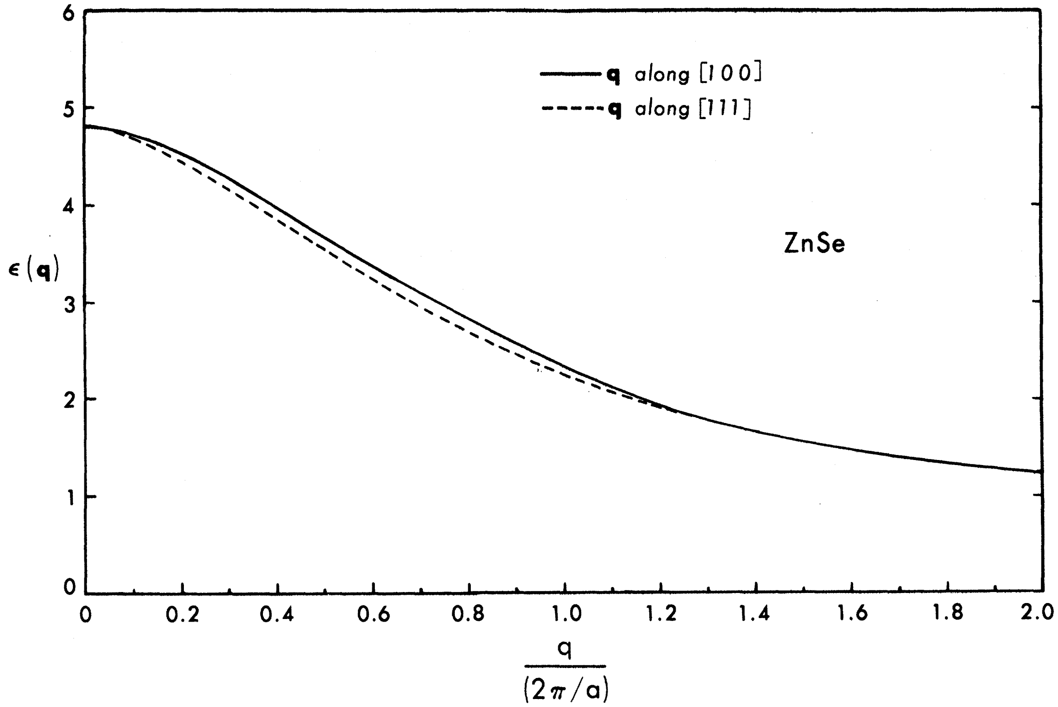

FIG. 5. Calculated microscopic dielectric function of ZnSe along two symmetry directions. $\epsilon(\vec{q})$ for $\vec{q}$ along [110] is essentially the same as for $\vec{q}$ along [100].

where V_a and V_b are the properly screened pseudopotentials for the Si atoms and the bonding charges, respectively, and S_b/S_a is the ratio of the structure factors of the bonding charges to the Si atoms.

$V_a(G_1)$ is just equal to Animalu and Heine's value of -0.18 Ry corrected by a factor $X_f(G_1)/X(G_1)$. Therefore, $V_a(G_1) = -0.18(1.76/1.33) = -0.238$ Ry. $V_b(q)$ may be calculated from Poisson's equation:

$$V_b(q) = (4\pi e/\Omega q^2)8e/\epsilon(0) .$$

The exchange correction reduces $V_b(G_1)$ by a factor of 0.77. Thus we have $(S_b/S_a)V_b(G_1) = 0.031$ Ry. Consequently,

$$V_p(G_1) = -0.238 + 0.031 = -0.207 \text{ Ry} .$$

This value is in excellent agreement with the value of $V_p(G_1) = -0.21$ Ry obtained by Brust, Cohen, and Phillips.[9]

We can make similar arguments for germanium. $V_a(G_1)$ is equal to Animalu and Heine's value of -0.19 Ry, corrected by a factor $X_f(G_1)/X(G_1)$, which gives $V_a(G_1) = -0.251$ Ry. V_b is reduced because $\epsilon(0) = 15.8$ for Ge, and thus $(S_b/S_a)V_b(G_1) = 0.022$ Ry. Consequently,

$$V_p(G_1) = -0.251 + 0.022 = -0.229 \text{ Ry}.$$

This value is in excellent agreement with the value of $V_p(G_1) = -0.23$ Ry obtained by Cohen and Bergstresser.[2]

It should be noted that the comments by Srinivasan[4] on Nara's results do not hold for our results. We have used a large number of interband transitions $(1-4) \rightarrow (5-15)$ in our calculations. The convergence at large q is satisfactory in view of the very small contribution to $\epsilon(q)$ from the transitions $(4 \rightarrow 14)$, $(4 \rightarrow 15)$, etc. Furthermore, our value of $\epsilon(0) = 11.3$ is obtained without the necessity of adding more sampling points for the case $q = 0$.

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

[2] M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966); J. P. Walter and M. L. Cohen, *ibid.* 183, 763 (1969).

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

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

[5] H. Nara, J. Phys. Soc. Japan 20, 778 (1965); 20, 1097 (1965).

[6] R. M. Martin, Phys. Rev. Letters 21, 536 (1968).

[7] J. C. Phillips, Phys. Rev. 166, 832 (1968).

[8] A. Morita and H. Nara, J. Phys. Soc. Japan Suppl. 21, 234 (1966).

[9] The pseudopotential form factors are taken from the following papers: Si: D. Brust, M. L. Cohen, and J. C. Phillips, Phys. Rev. Letters 9, 389 (1962); Si and Ge: M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966); Si and GaAs: R. R. L. Zucca, J. P. Walter, Y. R. Shen, and M. L. Cohen, Solid State Commun. 8, 627 (1970); ZnSe: J. P. Walter, M. L. Cohen, Y. Petroff, and M. Balkanski, Phys. Rev. B 1, 2661 (1970).

[10] Unpublished results of calculations done in conjunction with the published papers of Ref. 9.

[11] M. Renninger, Acta Cryst. 8, 606 (1955).

[12] W. C. Dunlop, Jr., and R. L. Watters, Phys. Rev. 92, 1396 (1953).

[13] K. G. Hambleton, C. Hilsum, and B. R. Holeman, Proc. Phys. Soc. (London) 77, 1147 (1961).

[14] E. Bernstein, in Proceedings of the Conference on the Physics of Semimetals and Narrow Gap Semiconductors, Dallas, 1970 (unpublished).

[15] A. O. E. Animalu and V. Heine, Phil. Mag. 12, 1249 (1965).

[16] V. Heine and I. Abarenkov, Phil. Mag. 9, 451 (1964).

[17] J. Hubbard, Proc. Roy. Soc. (London) A243, 336 (1958).