

# First-Principles Calculation of the Optical Absorption in Diamond\*

A. R. Lubinsky and D. E. Ellis<sup>†</sup>

*Physics Department, Northwestern University, Evanston, Illinois 60201*

and

G. S. Painter

*Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830*

(Received 23 March 1972; revised manuscript received 5 July 1972)

A nonempirical first-principles energy-band calculation for diamond has been used to calculate the optical absorption expressed as the imaginary part of the complex dielectric function  $\epsilon_2(\omega)$  in the random-phase approximation. The use of  $\mathbf{k}$ -dependent transition-probability matrix elements calculated from the Bloch linear-combination-of-atomic-orbitals wave functions is found to significantly improve agreement of the calculated  $\epsilon_2(\omega)$  with experiment, as compared to the results obtained with averaged matrix elements. Within the statistical exchange one-electron band model Hamiltonian and the random-phase approximation to the dielectric function, we find good agreement with experiment for the magnitude and position of the main peak and general shape of  $\epsilon_2(\omega)$  over a large energy range without any empirical adjustment of the calculation. There is structure in the low-energy region which is not reproduced by our treatment, suggesting inherent deficiencies of the band model and/or limitations of the theoretical expression for  $\epsilon_2(\omega)$ .

## I. INTRODUCTION

Although the energy-band structure of diamond has been the subject of considerable study,<sup>1</sup> the theoretical calculations have generally proved too inaccurate to provide a completely satisfactory interpretation of the observed optical spectrum. Recently more refined experimental procedures and the development of band-theory techniques capable of including "non-muffin-tin" corrections to the crystal Hamiltonian have made it possible to compare the results of theory and experiment over a large energy range<sup>2,3</sup> for solids characterized by strongly anisotropic crystal potentials. The optical properties of insulators present an important test for theoretical models of electronic structure. Expressed as the imaginary part of the dielectric function  $\epsilon_2(\omega)$ , the optical absorption provides a convenient measurable quantity to be compared with model predictions. Detailed comparisons of this sort, when based on first principles or *ab initio* band structure models, can reveal the inherent shortcomings of the theoretical models of excitations in insulators, and help resolve important questions concerning many-body effects on the dielectric function.

Furthermore, first-principles calculations of  $\epsilon_2$  provide a check and "calibration" point for improving pseudopotential and other empirical schemes, in which various features of the band model and experimental data can be made to agree by proper choice of adjustable band parameters. The empirical-pseudopotential method has been used to calculate  $\epsilon_2$  in diamond by Saravia and Brust,<sup>4</sup> and more recently by Hemstreet, Fong, and Cohen,<sup>5</sup>

who used a nonlocal-empirical-pseudopotential model (NEPM). The earlier pseudopotential calculations do not yield very good agreement with the position of the main peak in the experimentally derived  $\epsilon_2$ , nor with the line shape at lower energies. The NEPM results are in good agreement with the position of the main peak in type-I diamond, but are based on a band structure with a level ordering different from that found in the first-principles calculations. Furthermore, there is a large discrepancy with experiment for the magnitude of the main peak in  $\epsilon_2$ , and the band results predict additional structure which is not found in the experimental curve.

In this article we report a calculation of  $\epsilon_2$  obtained directly from a first-principles Hartree-Fock-Slater one-electron treatment of the band structure of diamond and investigate the correspondence with experiment. The band structure was calculated using the discrete variational method<sup>6</sup> (DVM) in a linear-combination-of-atomic-orbitals (LCAO) Bloch basis set, as reported in a recent paper.<sup>7</sup> The assumed potential function used in that work was formed by the superposition of atomic Coulomb potentials and charge densities employing the statistical exchange approximation without any empirical adjustment to experimental data. Previous success in correlating features of the theoretical DVM band structure of graphite<sup>3</sup> and diamond with experiment motivates this more extensive first-principles calculation of  $\epsilon_2$ . In diamond the DVM results were in excellent agreement with the best-known experimental detail of the band structure, the indirect-transition threshold, and calculations of the interband densities of

states showed encouraging correspondence with the experimental  $\epsilon_2$  spectrum. Structure in the optical absorption has been generally interpreted in terms of critical points of the interband density; however, a proper treatment requires the calculation of oscillator strengths contributing to  $\epsilon_2$  from the entire Brillouin zone. A major goal of this work has been to investigate the behavior of the oscillator strengths and to determine their role in shaping  $\epsilon_2$ .

We calculate the interband contribution to the imaginary part of the dielectric function<sup>8</sup>:

$$\epsilon_2(E) = A \sum_{i,j} \frac{1}{(2\pi)^3} \int d\vec{k} f_{ij}(\vec{k}) \frac{\delta(E_{ji}(\vec{k}) - E)}{E_{ji}(\vec{k})}, \quad (1)$$

where

$$f_{ij}(\vec{k}) = \frac{2|\langle \vec{k}, i | p | \vec{k}, j \rangle|^2}{3m E_{ji}(\vec{k})} \quad (2)$$

is an interband oscillator strength between valence band  $i$  and conduction band  $j$  at a given point  $\vec{k}$  in the Brillouin zone,  $E_{ji}(\vec{k})$  is the corresponding energy difference, and  $A = e^2 \hbar^2 / m$ . Scattering, relaxation effects, and local-field corrections are not included in this expression for  $\epsilon_2$ . We calculate the singular integrals appearing in (1) in a histogram representation by interpolating the  $\vec{k}$ -dependent oscillator strengths and energies throughout the Brillouin zone and integrating numerically by irrational vector sampling.<sup>7</sup>

## II. RESULTS

In order to calculate the integrals of Eqs. (1) and (2), it is necessary to choose a representation of  $E(\vec{k})$  and  $f_{ij}(\vec{k})$  over the entire Brillouin zone based on the finite number of "data points" available from a first-principles calculation. Semiempirical Fourier-series representations have been much used in the past in a variety of applications. These applications include the LCAO "tight-binding" procedure of Slater and Koster<sup>9</sup> where empirical atom-atom interactions were deduced, and the effective-mass Hamiltonian scheme of Dresselhaus and Dresselhaus.<sup>10</sup> A Fourier-series band representation was selected for this work; however, for our purposes, some other interpolation functions (e.g., Kubic harmonics or local interpolation, see below) would serve as well. The convergence properties and error analysis of the Fourier expansions used here are discussed in more detail in the Appendix.

Fourier representations of each of the four valence bands and each of the lowest set of conduction bands were obtained in a least-squares fit over 45 inequivalent wave vectors using symmetrized sums of plane waves<sup>11</sup> for the fitting functions  $F_s(\vec{k})$ . Numbering individual energy-band representations in order of increasing energy, the  $j$ th energy band appears as

$$\bar{E}_j(\vec{k}) = \sum_{s=1}^S b_s^j F_s(\vec{k}). \quad (3)$$

With  $S = 25$ , we were able to attain fits to the energy bands with root-mean-square (rms) errors of approximately  $3 \times 10^{-3}$  a.u. in the valence bands and  $6.5 \times 10^{-3}$  a.u. in the conduction bands. By numerically evaluating the matrix elements of the gradient between the linear combinations of Bloch basis functions which form the solutions of the eigenvalue problem, the oscillator strengths were determined without the usual decomposition into atomic-multicenter integrals. Having found the oscillator strength for 16 valence-band-conduction-band pairs at 33 nondegenerate wave vectors in the Brillouin zone, additional matrix elements were calculated by local interpolation<sup>12</sup> of the form

$$\bar{f}_{ij}(\vec{k}) = \sum_{m=1}^M \omega_m f_{ij}(\vec{k}_m) / \sum_{m=1}^M \omega_m, \quad (4)$$

where the vectors  $\vec{k}_m$  denote the  $M$  given data points nearest to  $\vec{k}$ , and the weight  $\omega_m$  is given by

$$\omega_m(|\vec{k} - \vec{k}_m|) = |\vec{k} - \vec{k}_m|^{-3}.$$

In a histogram representation, we write

$$E \epsilon_2(E) = \sum_n C_n H_n(E),$$

where  $H_n(E)$  is a histogram function centered at energy  $E_n$ . Using the  $\vec{k}$ -interpolated oscillator strengths and energies from (3) and (4),

$$C_n = A V_a^{-1} \sum_{i,j} \frac{1}{N \Delta E} \sum_{i=1}^N \bar{f}_{ij}(\vec{k}_i) \Delta_{ji}^n(\vec{k}_i), \quad (5)$$

where  $\Delta_{ji}^n(\vec{k}_i)$  is unity if  $\bar{E}_{ji}(\vec{k}_i)$  is within an interval  $\Delta E$  (the histogram box width) about  $E_n$ , zero otherwise, and the vectors are the elements of the irrational vector sample over the Brillouin zone. In these calculations, we used  $\Delta E = 0.02$  a.u. and  $N = 25\,000$  sample points to give an energy resolution of approximately 0.3 eV in  $\epsilon_2$ .

A simplification often made in treating the dielectric function is to assume that the oscillator strengths (or gradient matrix elements) given in (2) are slowly varying functions of  $\vec{k}$  and to replace them with some average  $\bar{f}_{ij}$ :

$$E \epsilon_2 = A \sum_{i,j} \bar{f}_{ij} I_{ij}(E). \quad (6)$$

For example, we may define a volume average according to

$$\bar{f}_{ij} = V_k^{-1} \int d\vec{k} f_{ij}(\vec{k}),$$

or we may consider these average oscillator strengths as adjustable parameters. The  $I_{ij}(E)$  are the interband densities of states given by

$$I_{ij}(E) = \frac{1}{(2\pi)^3} \int d\vec{k} \delta(E_{ji}(\vec{k}) - E). \quad (8)$$

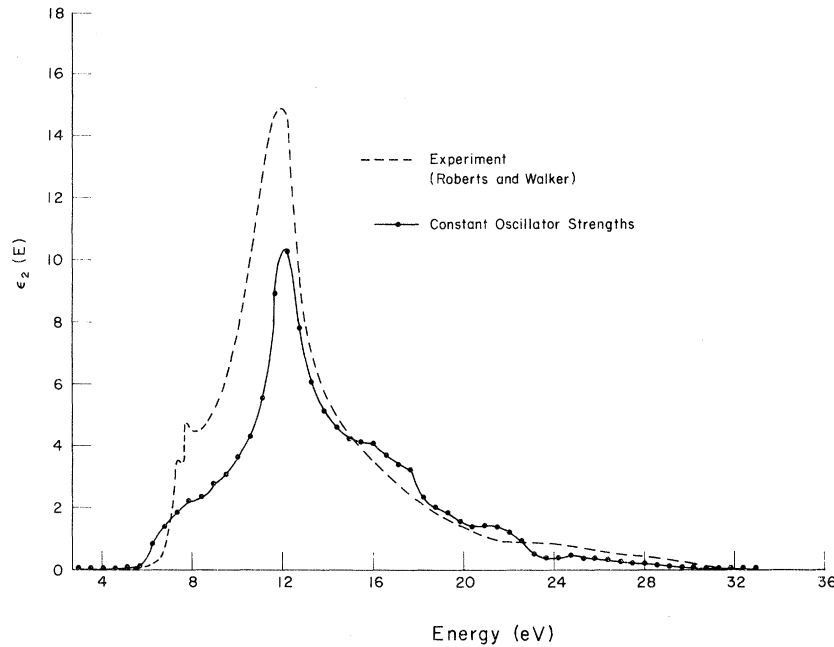


FIG. 1. Comparison of experimental  $\epsilon_2$  with theory:  $\vec{k}$ -averaged oscillator-strength approximation.

Critical points<sup>13</sup> can give rise to four types of analytic singularities in the interband densities. It is in terms of these Van Hove singularities arising from single critical points that structure in the optical spectra is often interpreted, and one of our purposes is to determine the adequacy of such analysis. In Fig. 1 we present the results of a calculation of  $\epsilon_2$  in the approximation (6) of using  $\vec{k}$ -averaged oscillator strengths. Contributions from 16 interband pairs between the four highest valence bands and the four lowest conduction bands were considered. The experimental curve appearing in Fig. 1 is from the paper of Roberts and Walker.<sup>14</sup> Although the position of the main peak is in fairly good agreement with experiment, its height is too low, both near the main peak and at lower energies, and structure arising from  $I_{46}(E)$ , which is not observed in the experimental curve, appears at higher energies (15–18 eV). It is evident that the constant-oscillator-strength approximation leads to significant disagreement with the experimental  $\epsilon_2$ .

To further investigate the effects of the constant-matrix-element approximation, it is convenient to cast the oscillator strengths into an explicitly energy-dependent form,

$$f_{ij}(E) = \frac{\int d\vec{k} f_{ij}(\vec{k}) \delta(E_{ji}(\vec{k}) - E)}{\int d\vec{k} \delta(E_{ji}(\vec{k}) - E)}. \quad (9)$$

The expression (1) for  $\epsilon_2$  may then be written in the equivalent form

$$E\epsilon_2(E) = A \sum_{i,j} f_{ij}(E) I_{ij}(E). \quad (10)$$

A calculation of the quantities in (8) and (9) was

made, and in Fig. 2 we show the results for band pairs 4–5 and 4–6, which are the most important contributors to  $\epsilon_2$  in diamond. It is seen that  $f_{45}(E)$  falls well below the  $\vec{k}$ -averaged 4–5 oscillator strength except in the vicinity of 12 eV. Also, the 4–5 interband density of states has a very large peak near 12 eV, indicating that states in an extended region of the Brillouin zone are participating in transitions at these energies. Including the  $\vec{k}$  dependence of the 4–5 oscillator strengths will then effect an increase and sharpening of the main  $\epsilon_2$  peak. In the case of 4–6 transitions, it is seen that  $f_{46}(E)$  is decreasing rapidly at those energies where the interband density of states is large. The energy-dependent oscillator strength appears in this case to have at least as much structure as the interband density itself, and will significantly affect the contribution to  $\epsilon_2$  from this band pair. For example, although  $I_{46}(E)$  has a sharp edge near 17–18 eV, the oscillator strengths are falling to a minimum at these energies, and their inclusion in the final calculation will greatly reduce the comparative strength of this structure in  $\epsilon_2$ .

In Fig. 3 we present the results of a full calculation of  $\epsilon_2(E)$  according to (10) with  $\vec{k}$ -dependent matrix elements (2) included. Experimentally, structure in  $\epsilon_2$  for type-IIa diamond is observed at 7.3, 7.8, 12.2, 16, and 23 eV. The main feature of the optical absorption is the large peak at 12.2 eV. The 7.8-eV peak is strongly temperature dependent, and the situation regarding structure at 16 eV is unclear. Earlier workers<sup>15</sup> observed it, but Roberts and Walker find no sharp structure near

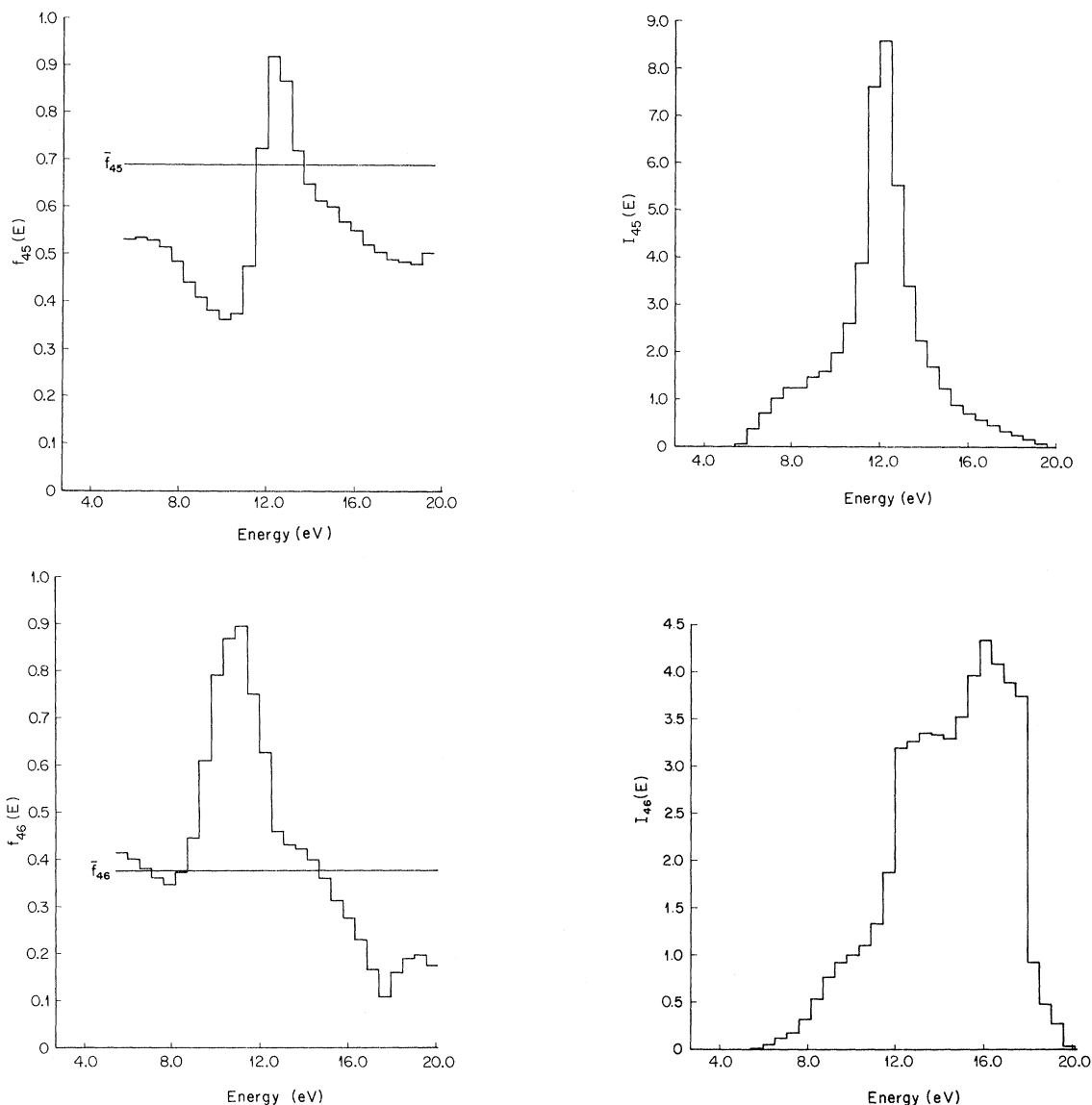


FIG. 2. Energy-dependent oscillator strength and interband density of states for 4-5 and 4-6 band pairs.

this energy. However they caution that their data are least reliable between 13 and 19 eV. The main peak in the theoretical curve is at  $12.25 \pm 0.3$  eV. In a previous paper<sup>7</sup> we gave an analysis of structure in  $\epsilon_2$  in terms of critical transitions at symmetry points and along symmetry lines. Strong contributions to the main peak come from the transitions  $L_{3'}-L_3$  (12.0 eV),  $L_{3'}-L_1$  and  $X_4-X_1$  (12.5 eV), including transitions along  $\Sigma$  to the  $K$  point (12.1 eV). It should be emphasized however that the over-all size and shape of  $\epsilon_2$  result from transitions over an extended region in  $\vec{k}$  space. We find that 4-5 transitions account for about 65% of the peak height, with 4-6 and 3-5 transitions con-

tributing about 10% each. The calculated direct threshold is at about 6.0 eV, arising from 4-5 zone-center transitions ( $\Gamma_{25'} - \Gamma_{15}$ ). We find a weak change in slope in the theoretical  $\epsilon_2$  at  $8.4 \pm 0.3$  eV which is due to a shoulder in the 4-5 contribution. Another weak change in slope occurs at  $16.6 \pm 0.5$  eV, arising from 4-6 transitions. Finally, the theoretical curve falls below the experimental one for energies above about 22 eV. In the DVM energy-band calculation, a second set of conduction bands was found which will begin to contribute to the optical absorption with small oscillator strengths above about 20 eV. These states were not included in the present calculation of  $\epsilon_2$ .

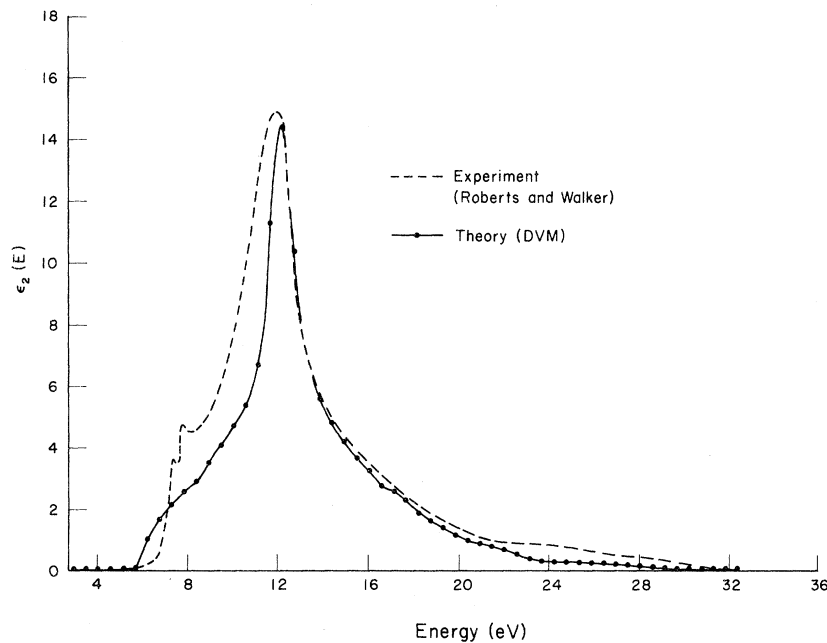


FIG. 3. Comparison of experimental  $\epsilon_2$  with theory:  $\vec{k}$  dependence of oscillator strengths included.

### III. DISCUSSION

We find that the  $\epsilon_2$  calculated directly from the DVM energy-band structure and wave functions without empirical adjustment agrees quite well with the experimental curve for diamond with regard to the position of the main peak and general shape over a wide energy range. The most important discrepancies between theory and experiment involve the shape of the calculated absorption edge near the direct threshold and the fact that the calculated  $\epsilon_2$  is systematically lower than the experimental curve on the low-energy side of the main peak. Including the  $\vec{k}$  dependence of the oscillator strengths leads to improved agreement with experiment; previous investigations based on pseudopotential wave functions have left this point somewhat uncertain. Thus, Brust finds<sup>16</sup> an  $\epsilon_2$  for Si which is insensitive to  $\vec{k}$  averaging, while Herman *et al.*<sup>17</sup> report considerable sensitivity in a similar study of Ge.

Concerning the significant disagreement between experiment and the theoretical  $\epsilon_2$  curve between threshold and approximately 12 eV, we consider the following possible causes: (a) errors in oscillator strengths and/or band structure, (b) local-field effects, and (c) exciton modes.

Estimation of absolute errors in the oscillator strengths calculated from *approximate* solutions to the band problem is difficult. As is well known from molecular theory, the use of approximate eigenfunctions of the Schrödinger equation (although accurate according to the energy criterion) can lead to large uncertainties in the calculated

oscillator strengths. Thus, it is desirable to carry out systematic studies of  $f_{ij}(\vec{k})$  as derived from various band models.<sup>18</sup> In the present case, however, we consider that the shape of the theoretical  $\epsilon_2$  curve near threshold, which is in significant disagreement with experiment, cannot be seriously affected by errors in the oscillator strengths, since this shape is evident even in the constant-oscillator-strength approximation.

It appears that carrying the band-structure calculation through to self-consistency would not significantly alter the calculated  $\epsilon_2$ , since the *ad hoc* starting crystal charge density obtained by superimposing free-atom Hartree-Fock-Slater charge densities is matched very closely by that calculated from the Bloch solutions to the resulting model Hamiltonian. Also, these results are not expected to depend strongly on the exchange factor since the variation of the band gaps with exchange scaling is relatively slight in diamond.<sup>7</sup>

In addition to the various optical energy-gap comparisons of the first-principles band structure put forward in our previous article,<sup>7</sup> we can also use cyclotron effective masses to investigate band parameters around the  $\Gamma$  point. Lacking reliable effective-mass data for both valence and conduction bands, the light-hole, heavy-hole, and third-band-hole masses obtained by Rauch<sup>19</sup> for type-IIIb semiconducting diamond was compared with our calculated valence-band structure. The calculated effective masses are considerably smaller than the experimental values. Further experimental studies which can distinguish between (intrinsic) conduction-band and impurity-band resonances would be

helpful. However, we see that even modification of our band structure to fit the available  $m^*$  data (which would increase the slope of the absorption edge) would not alter the essential conclusion that the calculated line shape of absorption at low energies is qualitatively different from experiment.

There is the interesting possibility that local-field (or Lorentz) corrections<sup>20,21</sup> to the theoretical form of the dielectric function (1) can affect the shape of the theoretical curve; in a tight-binding model their inclusion would increase the value of the calculated  $\epsilon_2$  on the low-energy side of the main peak, thus at least partially resolving the systematic deviation from experiment which is observed in this energy range.<sup>22</sup>

The peaks in the experimental absorption at 7.3 and 7.8 eV require further study. We tentatively identify the temperature-independent 7.3-eV peak with a change in slope in the 4–5 interband density of states, which appears at about 7.5 eV in our calculation. This feature would appear as a weak bit of structure in a higher-resolution calculation of  $\epsilon_2$ . Temperature-dependent structure in the low-energy absorption has previously been ascribed either to energy-band shifts, or to exciton modes<sup>23</sup>; we find no feature of the band structure to support the former hypothesis. Furthermore, inspection of our theoretical band structure along symmetry lines shows no regions which will support direct ( $\vec{k}$  conserving) excitons with a reasonable binding energy. In fact we find only one region, valence-band states around  $L$  coupled to conduction-band states along  $\Delta$ , which appears capable of supporting an *indirect* exciton of this energy. Such an assignment is purely speculative; line-shape studies of the 7.8-eV peak would be valuable. Van Dyke has recently made a study of interband absorption in Si and Ge using the orthogonalized-plane-wave (OPW) method<sup>18</sup>; he concludes that the 3-eV peak in Si similarly is due to excitonic effects.

The absolute magnitudes of the calculated oscillator strengths are subject to a further check through the sum rule on  $\epsilon_2$ ;

$$\int_0^\infty \omega \epsilon_2(\omega) d\omega = \frac{1}{2} \pi \omega_p^2,$$

which can be written in the form

$$\int_0^{\omega_0} \omega \epsilon_2(\omega) d\omega = \frac{1}{2} \pi (4\pi N e^2 / m) n(\omega_0), \quad (11)$$

where  $N$  is the atom density and  $n(\omega_0)$  represents an effective number of electrons/atom contributing to the optical properties in the frequency range  $0-\omega_0$ . By integrating the theoretical  $\epsilon_2$  over the range  $0-38$  eV, or by adding the averaged oscillator strengths  $\bar{f}_{ij}$ , we obtain  $n(38 \text{ eV}) = 2.2$  electrons/atom. Integrating the experimental  $\epsilon_2$  over the same frequency range gives approximate-

ly  $n(38 \text{ eV}) = 2.9$  electrons/atom. This result may be compared to the optical absorption in graphite, where  $n(\omega_0)$  reaches the saturated value of 4 electrons/atom at 30 eV.<sup>24</sup> More rigorous tests of the sum rule will require evaluation of the high-energy tail of  $\epsilon_2$ , including contributions from core levels and a large number of excited state bands.

#### APPENDIX: FOURIER REPRESENTATIONS OF ENERGY BANDS

Energy expansions in Fourier series in a restricted energy interval have been successfully used by Ketterson, Mueller, and Windmiller<sup>11</sup> and by Roaf<sup>25</sup> for fitting experimental (de Haas-van Alphen) Fermi-surface data in Pt and in the noble metals. Fourier representations of the energy bands of Fe were constructed and used to calculate the Fermi surface by Maglic and Mueller.<sup>26</sup> Using approximately 1000 symmetrized plane waves per band, they found an accuracy in energy of  $\approx 2$  mRy over the entire Brillouin zone. Schuurmans, van Haeringen, and Junginger<sup>27</sup> have investigated Fourier fitting the energy bands throughout the Brillouin zone in Si, GaAs, Al, and Pb. They considered fits to the energies at  $M$  data points using  $S$  symmetrized plane waves and calculated the average and maximum errors over another set of  $M'$   $k$  points. In band 3 of Si, for example, they found average errors of 3.5 and 2.0 mRy for  $S=20$  and 30, with  $M=200$ . In band 5, they found average errors of 7.2 and 6.3 mRy for  $S=20$  and 30. These values are about half the size of rms errors found by us in the corresponding bands of diamond with  $S=25$ , using a smaller number of fitting points. These authors emphasize that unwanted oscillations in these fits can occur, and they find maximum errors considerable larger than the average errors cited above.

Energy-band functions are continuous throughout the Brillouin zone, but can have discontinuous derivatives at points of degeneracy, which cannot be exactly reproduced by a finite Fourier series. For example, cross-over degeneracies occur in the conduction bands of diamond. These degeneracies lead to kinks in the band structure, which in turn will lead to unwanted oscillations in the Fourier representation. This behavior is further manifest in a reduced convergence rate of the Fourier coefficients measured by the number of plane waves required for given rms error. Naturally, it is undesirable to differentiate this series; however, our method of evaluating Eq. (1) by numerical integration is not susceptible to this type of error.

We find that increasing the number of Fourier coefficients  $S$  in the fit decreases the rms error and "more faithfully" reproduces structure visible

in hand-drawn plots of the data. At the same time, we do observe oscillations in the fit which appear "unphysical"; these oscillations become more pronounced as the number of fit functions approaches the number of given data points. This is a familiar phenomenon in fitting methodology. For a given number of data points  $M$ , an optimum

number of coefficients  $S$  is chosen such that the oscillatory behavior is kept to an acceptable level. Simultaneously we require that the rms level in fitted energy differences (the quantities required for calculations) should be equal to or less than approximately  $\frac{1}{3}$  of the energy resolution (histogram width) chosen for the  $\epsilon_2$  calculation.

\*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation, by the Air Force Office of Scientific Research, Grant No. 71-2012, and by the Advanced Research Projects Agency through the Northwestern University Materials Research Center.

<sup>†</sup>Alfred P. Sloan Research Fellow.

<sup>1</sup>F. Herman, R. L. Kortum, and C. D. Kuglin, *Internst. Quantum Chem.* **15**, 533 (1967).

<sup>2</sup>R. F. Willis, B. Feuerbacher, and B. Fitton, *Phys. Rev. B* **4**, 2441 (1971); B. Feuerbacher and B. Fitton, *Phys. Rev. Letters* **26**, 840 (1971).

<sup>3</sup>G. S. Painter and D. E. Ellis, *Phys. Rev. B* **1**, 4747 (1970).

<sup>4</sup>L. R. Saravia and D. Brust, *Phys. Rev.* **170**, 683 (1968).

<sup>5</sup>L. A. Hemstreet, Jr., C. Y. Fong, and M. L. Cohen, *Phys. Rev. B* **2**, 2054 (1970).

<sup>6</sup>D. E. Ellis and G. S. Painter, *Phys. Rev. B* **2**, 2887 (1970).

<sup>7</sup>G. S. Painter, D. E. Ellis, and A. R. Lubinsky, *Phys. Rev. B* **4**, 3610 (1971).

<sup>8</sup>H. Ehrenreich and M. H. Cohen, *Phys. Rev.* **115**, 786 (1959).

<sup>9</sup>J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954).

<sup>10</sup>G. Dresselhaus and M. S. Dresselhaus, *Phys. Rev.* **160**, 649 (1967).

<sup>11</sup>J. B. Ketterson, F. M. Mueller, and L. R. Windmiller, *Phys. Rev.* **186**, 656 (1969).

<sup>12</sup>P. J. Lin and J. C. Phillips, *Phys. Rev.* **147**, 469 (1966).

<sup>13</sup>L. Van Hove, *Phys. Rev.* **89**, 1189 (1953).

<sup>14</sup>R. A. Roberts and W. C. Walker, *Phys. Rev.* **161**, 730 (1967).

<sup>15</sup>W. C. Walker and J. Osantowski, *Phys. Rev.* **134**, A153 (1964).

<sup>16</sup>D. Brust, *Phys. Rev.* **139**, A489 (1965).

<sup>17</sup>F. Herman, R. L. Kortum, C. D. Kuglin, and J. L. Shay, in *International Conference on II-VI Semiconducting Compounds*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 503.

<sup>18</sup>J. P. Van Dyke, *Phys. Rev. B* **5**, 1489 (1972). A comparison of OPW and empirical-pseudopotential matrix elements is made for Si and Ge.

<sup>19</sup>C. J. Rauch, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, England*, edited by A. C. Stickland (The Institute of Physics and the Physical Society, London, 1962); *Phys. Rev. Letters* **7**, 83 (1961).

<sup>20</sup>S. L. Adler, *Phys. Rev.* **126**, 413 (1962).

<sup>21</sup>N. Wiser, *Phys. Rev.* **129**, 62 (1963).

<sup>22</sup>A recent study of local-field corrections based on a pseudopotential band model for diamond [J. A. Van Vechten and R. M. Martin, *Phys. Rev. Letters* **28**, 446 (1972)] indicates that their inclusion would have the opposite effect, however.

<sup>23</sup>J. C. Phillips, *Phys. Rev.* **139**, A1291 (1965).

<sup>24</sup>E. A. Taft and H. R. Philipp, *Phys. Rev.* **138**, A197 (1965).

<sup>25</sup>D. J. Roaf, *Phil. Trans. Roy. Soc. London* **A255**, 135 (1962).

<sup>26</sup>R. Maglic and F. M. Mueller, *Intern. J. Magnetism* **1**, 289 (1971).

<sup>27</sup>M. F. H. Schuurmans, W. van Haeringen, and H. -G. Junginger, *Solid State Commun.* **10**, 549 (1972).

## Lattice Dynamics of Cesium Chloride\*

A. A. Z. Ahmad,<sup>†</sup> H. G. Smith, N. Wakabayashi, and M. K. Wilkinson  
*Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830*

(Received 9 June 1972)

The phonon-dispersion curves have been measured for CsCl at 78 and 298°K on a triple-axis neutron spectrometer and analyzed in terms of a rigid-ion model and various shell models. A simple shell model with eleven parameters is sufficient to reproduce the measured dispersion curves. Frequency distributions and  $\omega_D$ -vs- $T$  curves were calculated based on the parameters determined from the two sets of data.

### I. INTRODUCTION

A considerable amount of theoretical work has been published by many authors on the lattice dy-

namics of the alkali halides with the NaCl and CsCl structures. At the beginning of the present study, experimental coherent inelastic neutron-scattering data had been obtained for numerous