Band Structure and Interband Optical Absorption in Diamond*

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In the present paper we compute the interband contribution to the imaginary part $\epsilon_2(\omega)$ of the dielectric constant in diamond. This is done for several model band structures. In particular, we conclude that either the present first-principles calculations have to be modified or there are extremely large many-particle corrections to the interband current near the fundamental ultraviolet absorption edge.

I. INTRODUCTION

THE energy bands of diamond have been subject to extensive theoretical studies.[1,2] In particular, Herman *et al.* have performed calculations which appear to have achieved, to a high degree, the requirements that the crystal potential be self-consistent. Herman's band structure was computed by an orthogonal-plane-wave (OPW) method, although recent calculations by Keown starting from an adjusted augmented plane wave (APW) have led to similar results.

On the experimental side, somewhat less is known about the band structure of diamond than for some of the other zinc-blende-type semiconductors. The indirect gap is known to be 5.4 eV with the minimum located on the Δ axis, about four-fifths of the way toward zone edge.[3,4] The threshold for direct interband transitions appears from the optical data [4–10] to be near 7 eV. Because there now exist good optical data,[4–10] we felt it worthwhile to compute the one-electron contribution to the optical absorption. We adopted the pseudopotential method for this purpose. Specifically, we were interested in determining whether the existing band structure could fit the $\epsilon_2(\omega)$ curve for diamond. Toward this aim we have chosen one model potential which places the important interband transitions at energies quite close to those deduced by Herman and by Keown. The results that follow from this model are quite surprising and are discussed below. In addition, we have examined several other models.

II. PROCEDURE

It is known from x-ray scattering data that in covalently bonded diamond a good deal of charge is localized in the bonds between nearest neighbors.[11,12] Theoretical studies have also demonstrated this.[13,14] Hence, we add to the pseudopotential a term to describe this effect. Such a potential has already been used by Saslow *et al.*[15] We then adjust this potential so as to give a level ordering at the symmetry points which is similar to that found by Herman and a reasonably similar band structure elsewhere. We did not attempt an exact fit, for reasons which are discussed below. In addition, we examined some other models in which we started with the Si potential[16] carried over to diamond by use of a scaling factor $(A_{Si}/A_C)^2$. Here A_{Si} and A_C are the lattice constants of Si and diamond, respectively. This was then slightly adjusted to put the principal levels in an order which we believe is required to explain the observed data on diamond if the single-particle interband current is used to interpret the optical experiments. That a definite ordering of levels is required will become apparent in the next two sections. Actually, one can readjust the potential coefficients slightly and get the same level ordering. No important changes are produced in the electronic spectra. Consequently, we only give results for one of these models below.

The zone sampling was done by a method described elsewhere.[17] In brief, we solve the pseudopotential secular equation at about 100 independent points. Then this is used in conjunction with a $\mathbf{k}\cdot\mathbf{p}$ truncation to give about 1600 points. Finally, this latter sample is used to generate a zone integration by a method similar to Gillat and Raubenheimer.[18] This method is extremely fast and gives extremely precise $\epsilon_2(\omega)$ curves. Actually, the accuracy is far better than needed in our present study.

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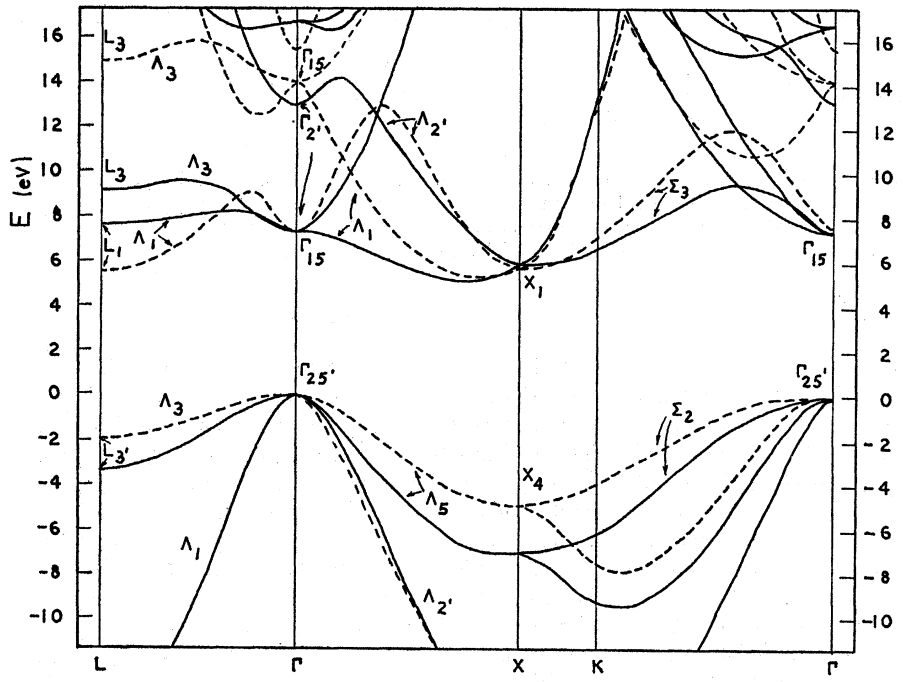

FIG. 1. Energy bands along some principal symmetry lines for models I (solid lines) and II (dashed lines).

III. RESULTS

The pseudopotential form factors, the principal energy gaps, and the position of the conduction-band minimum for both models are shown in Table I. The energy bands along the principal symmetry lines appear in Fig. 1. The computed values of $\epsilon_2(\omega)$ are shown in Fig. 2. Twelve interband transitions, from valence bands E_2, E_3, and E_4 to conduction bands E_5, E_6, E_7, and E_8, were considered. Experimental values[10] of $\epsilon_2(\omega)$ for diamond type IIa are also included in dashed lines.

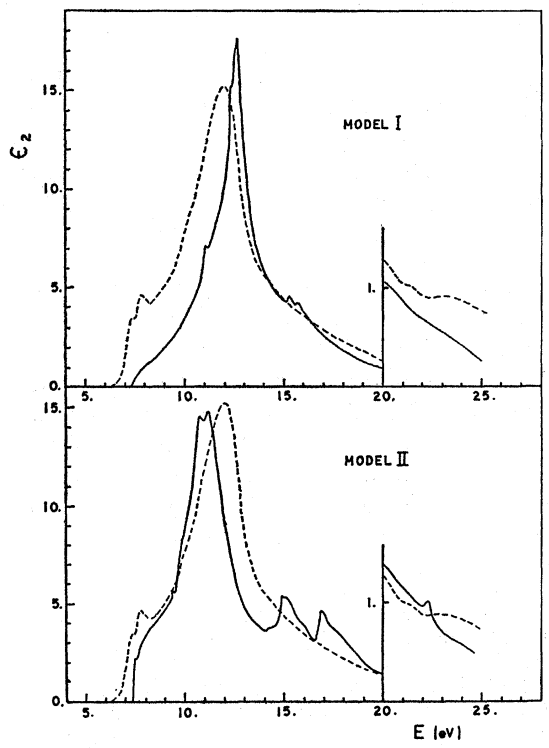

FIG. 2. Shows the contribution from twelve interband gaps to $\epsilon_2(\omega)$ for models I and II (solid lines). The experimental values for $\epsilon_2(\omega)$ are also shown (dashed lines). The values of $\epsilon_2(\omega)$ were calculated at intervals of 0.05 eV.

Model I will be studied first. The main contribution to ϵ_2 comes from the $E_{4,5}$ transitions. Its energy contours are shown in Fig. 3. The M_0 and M_1 critical points at Γ and L with energies of 7.33 and 10.88 eV, respectively, are clearly seen in $\epsilon_2(\omega)$. The large peak appears at 12.7 eV, and no critical point of importance is associated with it. It is produced by the contribution from an extended region in k space.

At large energies, the contribution to $\epsilon_2(\omega)$ comes mainly from the other interband transitions. The structure is very weak, and the only detectable change in slope appears at 15.25 eV. It is produced by the E_{4-6} interband transition and it is not associated with any important symmetry point but with an extended region. The interband transitions considered in this calculation do not produce any detectable structure at 23 eV.

For model II, the $E_{4,5}$ energy contours of the interband transition are shown in Fig. 4. The direct transition of lowest energy appears at the L point with an energy of 7.39 eV. There is a small segment, associated with this point, extending from the L point along the Λ line, where the energy varies only from 7.39 to 7.49 eV. This can be interpreted as a nearly two-dimensional critical point producing a step in $\epsilon_2(\omega)$ at 7.39 eV. At the Γ point there is another M_0 point with an energy of 7.52 eV. Although it is practically superimposed over

TABLE I. Theoretical values for the pseudopotential form factors, principal band gaps, and location of the conduction-band minimum of diamond. Some experimental values are included.

	V_{111}	V_{220}	V_{311}	V_{222}	$\Gamma_{25'}$-Γ_{15}	$\Gamma_{25'}$-$\Gamma_{2'}$	$L_{3'}$-L_1	X_4-X_1	$\Gamma_{25'}$-Δ_1	$\Delta_{\min}$
		(Ry)					(eV)			
Model I	−0.811	0.337	0.132	0.041	7.33	12.04	10.88	12.9	5.26	0.76
Model II	−0.514	−0.022	0.186	−0.078	14.06	7.52	7.39	10.43	5.37	0.83
Herman[a]					7.1	12.9	11.4	11.8	5.47	
Experiment								~12	5.47[b]	0.77[c]

[a] Reference 1. [b] Reference 4. [c] Reference 3.

the step, the change in slope indicates its presence. Other critical points indicated in Fig. 4 produce some weak structure related to the large peak and with changes of slope at 9.50 eV. The structure at higher energies comes from other interband transitions. The broad peaks at 15 and 17 eV are related to the E_{4-6} and E_{3-6} transitions, respectively. The contribution from E_{4-6} is not directly related to symmetry points but with volume effects. The contribution from E_{3-6} is directly related to the L transition which has an energy of 16.80 eV. The form of the peak is determined by critical points very near to that transition. Other models, not discussed here, show that the splitting of these peaks is very sensitive to small changes in the form factors. Only weak structure at 22.25 eV is visible near the experimental peak at 23 eV. It is produced by the E_{4-7} interband transitions.

IV. CONCLUDING REMARKS

We note that model I fails to explain the fundamental absorption edge in diamond. The leading edge near 7 eV is much too weak compared to experiment. This is quite puzzling as we note the band structure of model I is quite similar to Herman's OPW calculations. Particularly, the interband energies are really very close to Herman's throughout the zone, as demonstrated by Table I. Since it is known that the pseudopotential will give an extremely close fit to the OPW results, we can be confident that a whole-zone first-principles calculation would not differ much from our results of model I. Furthermore, it is also known that the APW predicts a band structure very similar to the OPW work.

It is clear why the optical absorption is so weak in model I. Examination of Fig. 3 discloses that only a small region of phase space near the zone center is contributing to the interband current, i.e., the reduced mass of the valence and conduction bands is much too small to make a strong phase-space contribution. Clearly the oscillator strength cannot be changed much as this would alter the form of the bands near Γ according to $\mathbf{k}\cdot\mathbf{p}$ theory, and furthermore it is known that the momentum matrix elements are given quite accurately

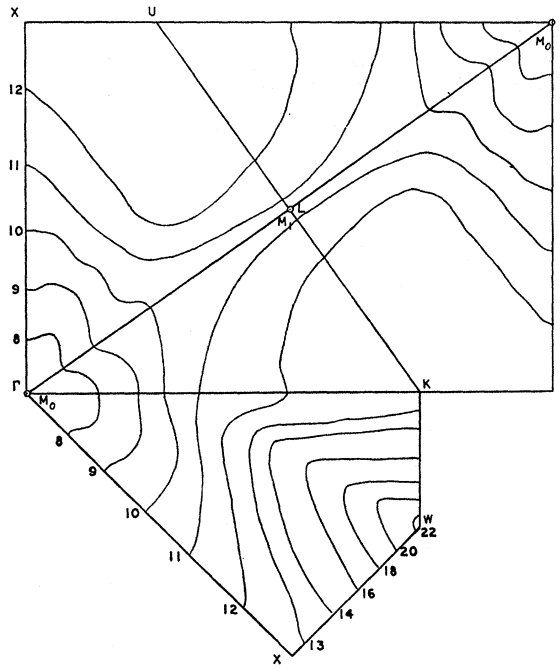

FIG. 3. $E_{4,5}(\mathbf{k})$ contours in eV for model I in the ΓKWL, ΓKL, and ΓXUL planes.

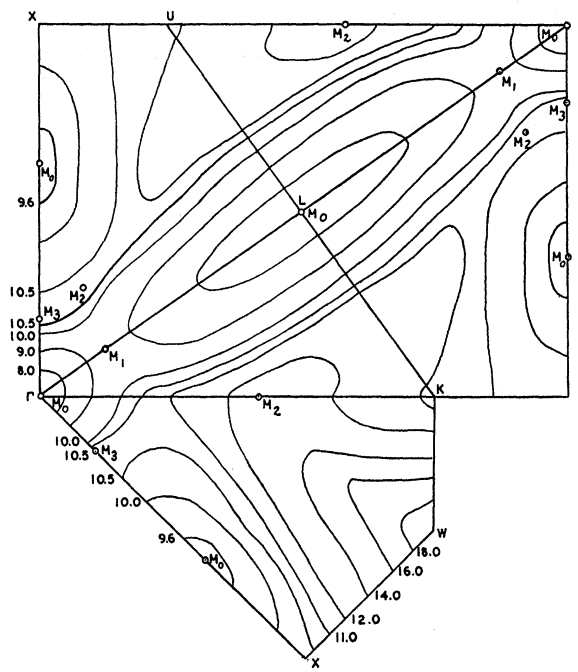

FIG. 4. $E_{4,5}(\mathbf{k})$ contours in eV for model II in the ΓKWL, ΓKL, and ΓXUL planes.

using the present size of secular determinant. It is clear from the band-structure diagram that there is no way that a small readjustment could remedy the situation. Thus we are forced to conclude that either the first-principles work is seriously in error for diamond or that there are important many-particle contributions to the fundamental optical edge.

We experimented with several other models which were intended to attempt to correct these discrepancies. We have found that bringing the $L_{3'} \rightarrow L_1$ transition down to about 7 eV improves the situation enormously. The best of several similar models is what we call model II in the present discussion. The difference in energy between the experimentally observed peak at 12 eV and ours near 11 eV is similar to what we found in an earlier result on Ge if the difference in scaling factor of 2.4 is noted. There is a slight disagreement between the position along the Δ axis of our conduction-band minimum and that determined by the neutron-diffraction studies in conjunction with radiation recombination measurements in diamond. This is seen in Table I. Presumably, all of the slight differences could be cleared up if we chose to add a k-dependent matrix element to the diagonal as done by Herman[19] in his fitting of the Ge band structure. In any case we would be interested in seeing the results of further first-principles studies on diamond as well as further experimental studies. In particular either electro-optic or piezo-optic measurements on the fundamental edge would be extremely helpful. According to model II we would expect diamond to show primarily L character in such a study. On the other hand, the presence of Γ transitions at the fundamental edge would lead to a fairly complex spectrum in a differential experiment near the fundamental edge if model I is the correct one. We also note the important qualitative differences between models I and II, namely, that in the first, L_1 is higher than Γ_{15}, whereas the situation is reversed in the latter. [*Note added in proof.* The reader may notice that the sign of $V(12)$ for model II is opposite from what would be expected from a self-consistent field point of view. This may, however, be associated with the fact that in effect we are here dealing with a renormalized potential rather than with the bare potential.[20]]

Finally, we comment on the structure near 16 eV which is present in both models, although it is much stronger in model II. The doublet is probably not significant as this splitting is hightly sensitive to the potential. The over-all strength of the structure near 16 eV, however, is not particularly sensitive to variation of the form factors. No account has been made of broadening in making the comparison between theory and experiment. To estimate the broadening factor results for the effect of electron-electron and electron-phonon scattering in diamond, we use our prior results in Si.[21] Taking proper account of the change of lattice and dielectric constant we find that the lifetime broadening in diamond should be $\sim\frac{1}{2}$ eV near $\hbar\omega=16$ eV. Thus, lifetime broadening will not wash out the structure at this energy. At the moment the experimental situation concerning the structure near 16 eV is somewhat unclear.

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