Local Pseudopotential Model for GaSb: Electronic and Optical Properties*

ROBERT N. CAHN† AND MARVIN L. COHEN
Department of Physics, University of California, Berkeley, California 94720
(Received 3 November 1969)

A local-pseudopotential calculation for GaSb using six form factors and one spin-orbit parameter has been found to give good agreement with the known features of the band structure. The reflectivity and wavelength-modulated reflectivity calculated using this band structure are in good agreement with experiment. All prominent features in the optical spectra can be identified with interband transitions in specific regions of the Brillouin zone.

INTRODUCTION

THE empirical pseudopotential method[1,2] (EPM) have been used to investigate the electronic band structure and optical properties of GaSb. This III-V semiconductor has been the subject of some controversy since the first EPM calculation of its band structure. At that time, Cohen and Bergstresser[1] noted that it was the least successful of the 14 semiconductor band structures they calculated. Since that time, an OPW calculation using three adjustment parameters,[3] a nonlocal pseudopotential calculation using six local, six nonlocal, and two spin-orbit parameters,[4] and a $k\cdot p$ calculation[5] have been done. Their relatively greater success cast doubt on the ability of the local pseudopotential method to account for the known features of the GaSb band structure. We have found, however, that modifying the Cohen-Bergstresser form factors by at most 0.03 Ry enabled us to reproduce all the electronic and optical properties of GaSb adequately. Spin-orbit interaction has also been included. The calculated reflectivity and modulated reflectivity are in good agreement with experiment. On this basis, we can confidently identify the sources of the observed optical structure. We have found that this identification is facilitated by examining interband energy contours in a particular plane in the Brillouin zone.

METHOD

The method of performing the energy-band calculations and computation of the complex frequency-dependent dielectric function have been described elsewhere.[1,2,6–9] The inclusion of the two-dimensional spin space doubles the matrix size which is approximately 60×60 (i.e., 30 plane waves for each spin); Löwdin's perturbation scheme[10] was used to reduce a matrix originally 240×240. We have used the Weisz spin-orbit scheme,[11] as modified by Bloom and Bergstresser.[12] The two spin-orbit parameters were constrained to have the same ratio as the splittings in the free atoms, leaving only one adjustable spin-orbit parameter. This was fixed to reproduce the known splitting of Γ_7^v-Γ_8^v at the top of the valence band. The optical properties were calculated in the manner described in Ref. 8.

We have sought to minimize the number of parameters involved in the calculation. In particular, no nonlocal parameters have been introduced. In the calculation of Cohen and Bergstresser,[1] the symmetric form factors were fixed by the values of the form factors for the column-IV semiconductors. Thus, their six form factors allowed only three parameters. We have relaxed this condition and allowed the symmetric form factors to vary slightly from the Cohen-Bergstresser values. Together with the inclusion of the spin-orbit interaction, this was sufficient to correct the recognized defects of their calculation. Our pseudopotential form factors were (in Ry)

$$V_3^S=-0.21,\quad V_8^S=0.015,\quad V_{11}^S=0.04,$$
$$V_3^A=0.09,\quad V_4^A=0.03,\quad V_{11}^A=0.01,$$

and the spin-orbit parameters were

$$\lambda_{Ga}=0.00065,\quad \lambda_{Sb}=0.00144.$$

BAND STRUCTURE

The experimental data on the band structure of GaSb have been summarized by Kosicki.[13] The spin-orbit

* Work supported by the National Science Foundation.
† National Science Foundation Graduate Fellow.
[1] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).
[2] D. Brust, Phys. Rev. **134**, A1337 (1964).
[3] F. Herman, R. L. Kortum, C. D. Kuglin, and J. P. Van Dyke, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic Press Inc., New York, 1968), Vol. 8, p. 193.
[4] H. I. Zhang and J. Callaway, Phys. Rev. **181**, 1163 (1969).
[5] C. W. Higginbotham, F. H. Pollak, and M. Cardona, in *Proceedings of the Ninth International Conference on the Physics of Semiconductors, Moscow* (Nauka, Leningrad, 1968), p. 57.
[6] W. Saslow, T. K. Bergstresser, C. Y. Fong, M. L. Cohen, and D. Brust, Solid State Commun. **5**, 667 (1967).
[7] Y. W. Tung and M. L. Cohen, Phys. Rev. **180**, 823 (1969).
[8] J. P. Walter and M. L. Cohen, Phys. Rev. **183**, 763 (1969).
[9] J. P. Walter, M. L. Cohen, Y. Petroff, and M. Balkanski (unpublished).
[10] P. Löwdin, J. Chem. Phys. **19**, 1396 (1951).
[11] G. Weisz, Phys. Rev. **149**, 504 (1966).
[12] S. Bloom and T. K. Bergstresser, Solid State Commun. **6**, 465 (1968).
[13] B. B. Kosicki, Technical Report No. HP-19, Harvard University, 1967 (unpublished).

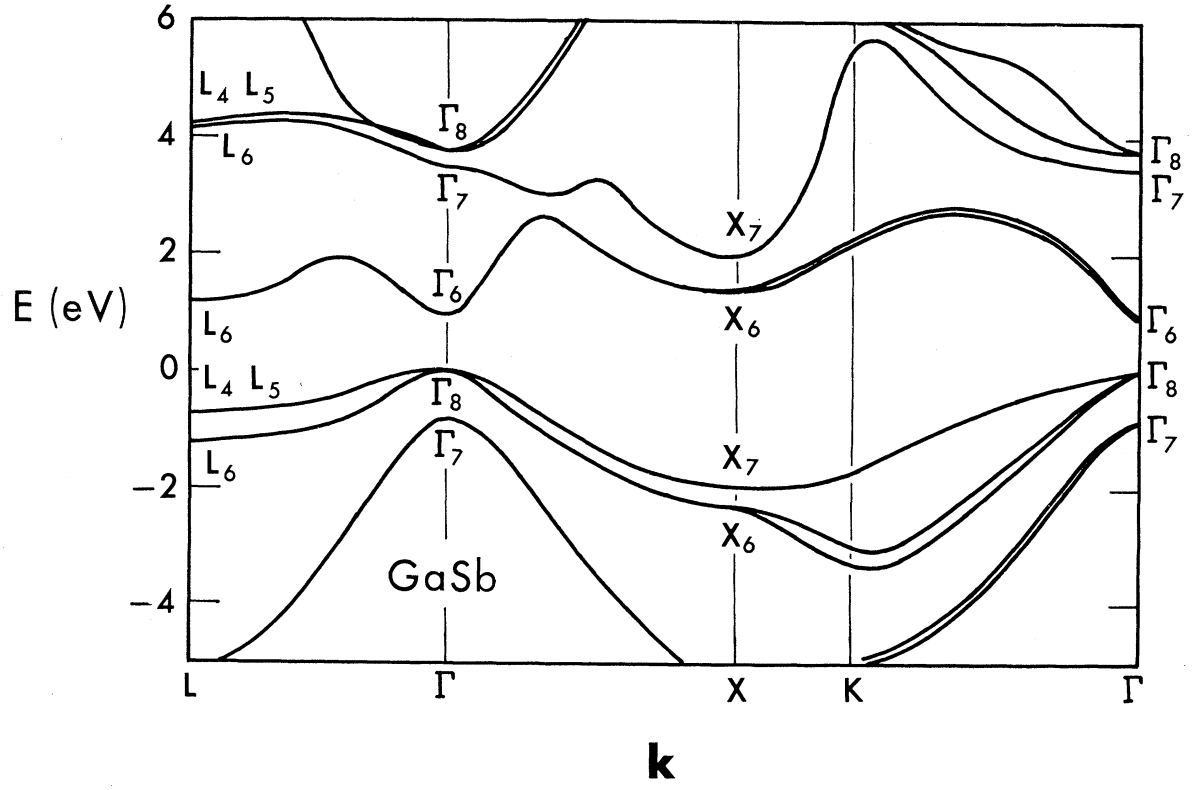

FIG. 1. The band structure of GaSb. Some bands slightly split by spin-orbit interaction are drawn as degenerate because of the smallness of the splitting.

splitting of Γ_{15}^v is 0.8 eV. The fundamental gap Γ_8^v-Γ_6^c is also 0.8 eV. The L_3^v-L_1^c is spin-orbit split with energies around 2.0 and 2.5 eV. The most distinctive feature is that the energies of the first conduction band at Γ, X, and L are nearly degenerate. Γ_6^c-L_6^c is 0.08 eV and Γ_6^c-X_6^c is 0.3 eV. It is these last two features which the Cohen-Bergstresser calculation failed to reproduce.

The present calculation (Fig. 1) reproduces most features of the known band structure to within 0.2 eV. In particular, the first direct gap Γ_8^v-Γ_6^c is 0.9 eV and the indirect gaps Γ_6^c-L_6^c and Γ_6^c-X_6^c are 0.28 and 0.48 eV, respectively. The spin-orbit splitting Γ_7^v-Γ_8^v is 0.8 eV. For $L_{4,5}^v$-L_6^c we find 1.93 eV and for L_6-$^vL_6^c$, 2.43 eV. The spin-orbit splitting along Λ is almost constant at 0.5 eV from L three-quarters of the way into Γ. The spin-orbit splitting along Δ is nearly constant at 0.35 eV from X three-quarters of the way in to Γ. We obtain 0.24 eV for the splitting of Γ_{15}^c.

INTERPRETATION OF SPECTRA

The optical properties of a material are determined by the complex dielectric function $\epsilon(\omega)$. The imaginary part of $\epsilon(\omega)$, $\epsilon_2(\omega)$ depends on the joint density of states and the momentum matrix elements. The Kramers-Kronig relation gives the real part of $\epsilon(\omega)$, $\epsilon_1(\omega)$ as an integral transform of the imaginary part.

For a given valence band and conduction band, the momentum matrix element is relatively constant through the zone. Thus, much of the observed optical structure can be understood in terms of the joint density of states.[2] A useful technique for approaching the joint density of states is to look for critical points[2,14] in the band structure throughout the Brillouin zone. These give rise to Van Hove singularities in the joint density of states and $\epsilon_2(\omega)$. Each of the four kinds of critical points contributes a characteristic feature to the shape of the ϵ_2 curve. The critical points are constrained by topological considerations to satisfy certain criteria.[15] In particular, the number of M_3 critical points plus the number of M_1 critical points must equal the number of M_2 critical points plus the number of M_0 critical points. In applying this, one must take into account the number of times a particular symmetry point or direction occurs within the zone. For the energy difference between the highest valence band and lowest conduction band, we find the following critical points and multiplicities:

M_0: $\Gamma(1)$, $\Delta(6)$, $X(3)$, $L(4)$,
M_1: $\Delta(6)$, $\Delta(6)$, $\Lambda(8)$,
M_2: $\Sigma(12)$,
M_3: $W(6)$.

[14] J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18.
[15] J. C. Phillips, Phys. Rev. **104**, 1263 (1956).

These satisfy all the required inequalities and the above stated equality. X and Δ are nearly degenerate and X may be an M_1 and there may be only one M_1 along Δ. These alternatives would also satisfy the rules for critical points. In addition, there may be nearly degenerate M_1's and M_2's in pairs in the flat region near K, with multiplicity 48.

Critical points guarantee only discontinuities in the derivative of ϵ_2. The actual size of a contribution to the spectrum depends on how much of the zone is dominated by a particular critical point. The density of states is related to the effective mass at the critical point. However, it is frequently the case that a contribution to ϵ_2 arises from a region so large that the effective-mass approximation is no longer valid. In this case, the contribution is best referred to as a volume effect, whether or not there is a critical point at approximately the same energy.

Volume effects are best understood by examining energy-difference contours.[2,16] This is usually done for the planes bounding a section of the Brillouin zone to which the symmetry operations can be applied to obtain the entire zone. In our case, this section contains 1/48 of the Brillouin zone,[2] inside which the band structure is actually calculated. A more revealing approach is to draw the contours for the plane determined by $\Gamma(0,0,0)$, $\Gamma(1,1,1)$, and $X(0,1,1)$. This plane contains $L(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $K(0,\frac{3}{4},\frac{3}{4})$. This latter point is K as referred to $\Gamma(0,0,0)$, but U as refered to $\Gamma(1,1,1)$. This plane contains the most interesting symmetry points, as well as the symmetry lines Λ, Δ, and Σ. The line from $\Gamma(1,1,1)$ to $U(0,\frac{3}{4},\frac{3}{4})$ is not equivalent to the line from $\Gamma(0,0,0)$ to $K(0,\frac{3}{4},\frac{3}{4})$ but the triangles ΓLK and ΓLU would be expected to contain rather similar energy contours since the contours must be identical along two of their three sides.

Figure 2 shows the contours for the energy difference between the highest valence band and the lowest conduction band. The critical polnts at Γ and L are immediately apparent. The M_1 critical point along Λ and the L critical point are parts of a long strip with energy difference between 1.90 and 2.20 eV (there is a spin-orbit split-valence band which contributes to a peak about 0.5 eV higher). A large plateau near K, including an M_2 along Σ, has energy difference 3.7 to 3.9 eV. This very extensive volume effect is responsible for the main peak which in GaSb occurs at about 4.2 eV in the reflectivity and slightly lower in ϵ_2 (Fig. 3).

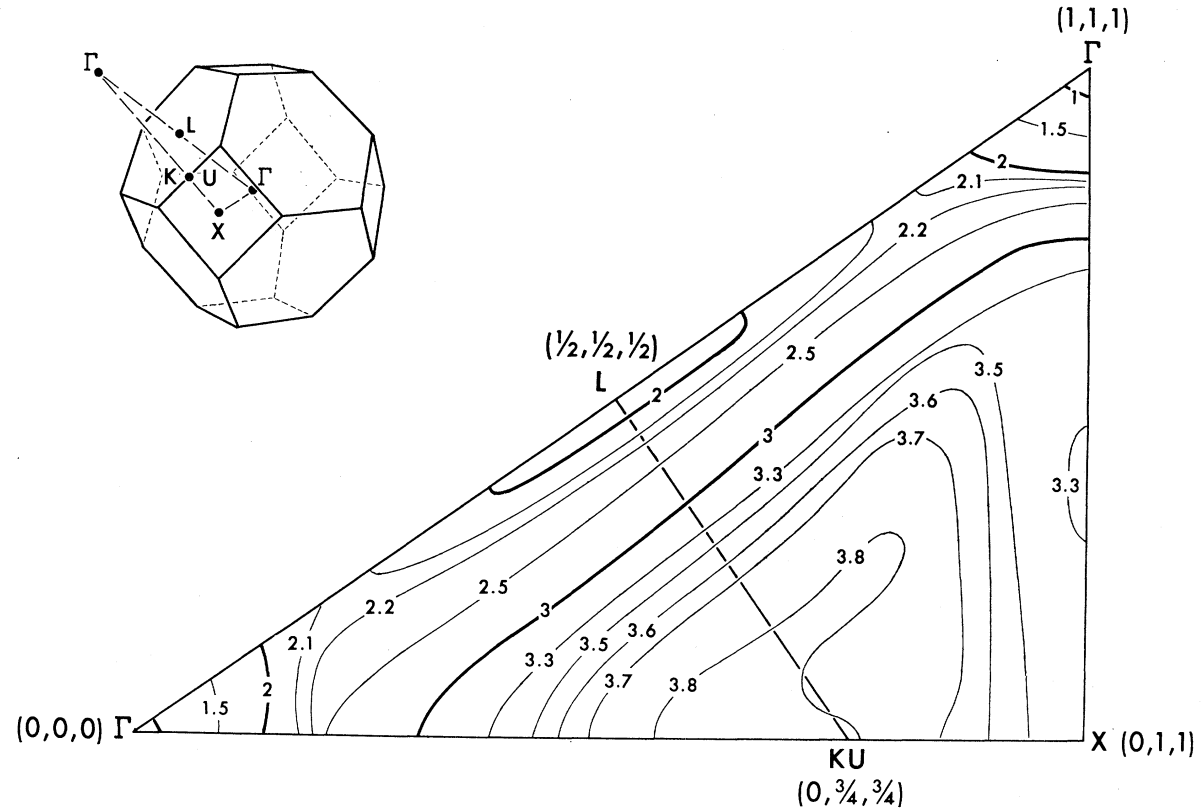

FIG. 2. Contours for the energy difference between the highest valence and lowest conduction bands.

[16] L. R. Saravia and D. Brust, Phys. Rev. 176, 915 (1968).

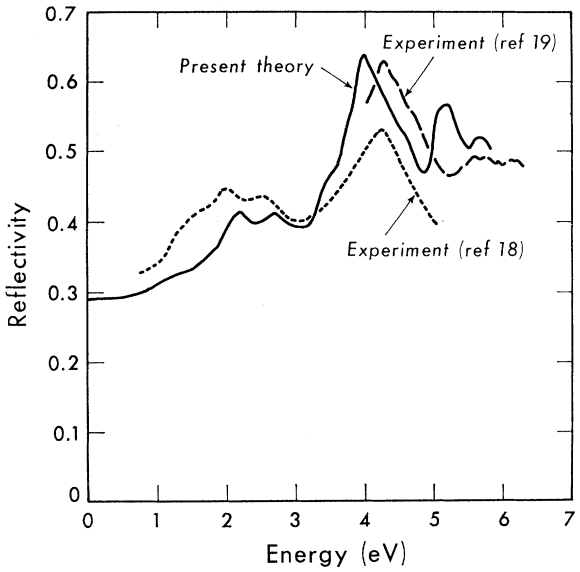

FIG. 3. The reflectivity of GaSb.

Finally, there is a relatively flat region just below 3.5 eV extending along Δ from X most of the way to Γ.

Reflectivity and modulated reflectivity measurements reveal structure at about 2.0, 2.5, 4.2, 5.6, and 6.1 eV and less well-defined structure between the 2.5 and 4.2 eV peaks[17–22] (Figs. 3 and 4). The first two peaks have been identified with the L-Λ region. The L_3^v level is spin-orbit split into L_6^v and $L_{4,5}^v$. Our results are in agreement with this assignment. The main peak at about 4 eV comes from the flat region near K (or U). The highest peaks are 4–6 (highest valence band, and second-lowest conduction band) transitions from a region including L. The splitting is again that of L_3^v since L_3^c splits very litte. Our calculated reflectivity (Figs. 4 and 5) is in good agreement with all these assignments except that our peaks are at 2.2, 2.7, 4.0, 5.2, and 5.7 eV.

The weak structure between the L doublet and the main peak is more controversial. It has been suggested that this is due to transitions near Γ. We find a significant structure at 3.5 eV in the reflectivity corresponding to a shoulder in ϵ_2 at 3.4 eV. Figure 5 shows this to be associated with transitions to the lowest conduction band. The flat region stretching from Δ through the zone (Fig. 2) is responsible for this structure. At this energy, the 4–6 transitions make only a 1% contribution to ϵ_2. The critical point for 4–6 transitions near Γ is significant in the 3.5–3.6-eV range, where the derivative of the reflectivity is lower than it is for 3.4–3.5 eV. Thus, we conclude that the Γ_{15}^v-Γ_{15}^c transitions do not contribute significantly to either the reflectivity or the derivative of the reflectivity. This may be traced to a density-of-states problem. Each Brillouin zone has only one Γ, but three X's, four L's, four K's, and eight U's. In addition to the 4-5 transitions, there is a contribution from 3–5 transitions about 0.3 eV higher. In our calculation, this is obscured by the main peak, whose position is too low by about 0.2 eV. The recent wavelength-modulated reflectivity of Zucca and Shen[22] shows two distinct structures which we believe can be attributed to the 4-5 and 3-5 transitions arising along Δ. Our interpretation of GaSb is nearly identical to the interpretation of the GaAs spectra given in Ref. 8.

Our band structure yields a main peak about 0.2 to 0.3 eV too low. The features above 4 eV are similarly lower than their counterparts in the experimental data. Attempts were made to rectify this situation by varying the local pseudopotential parameters. Because of the many constraints furnished by the known characteristics of the band structure and especially because of the unusual nature of the first conduction band referred to above, improvement of the high-energy structure resulted in the introduction of undesirable features at lower energy either in the band structure or in the calculated ϵ_2.

Our calculated ϵ_2 is compared with that of Zhang and Callaway in Fig. 6. The shapes of the curves are rather similar but the magnitude of the Zhang-Callaway result is larger by a factor of about 2. The scatter of the calculated points of Zhang and Callaway is greater because a coarser mesh was used in their calculation. In Fig. 4, our calculated reflectivity is compared to the

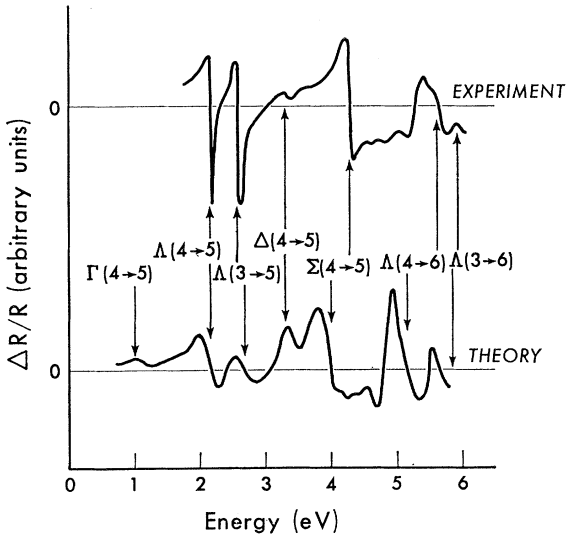

FIG. 4. The modulated reflectivity of GaSb. The experiment is that of Ref. 22.

[17] J. Tauc and A. Abraham, in *Proceedings of the International Conference on Semiconductor Physics, Prague* (Academic Press Inc., New York, 1960), p. 375.
[18] M. Cardona, J. Appl. Phys. Suppl. **32**, 2151 (1961).
[19] S. S. Vishnubhatla and J. C. Woolley, Can. J. Phys. **46**, 1769 (1968).
[20] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. **154**, 696 (1967).
[21] E. Matatagui, A. G. Thompson, and M. Cardona, Phys. Rev. **176**, 950 (1968).
[22] R. Zucca and R. Shen (unpublished).

experiments of Cardona, and Vishnubhatla and Woolley. The agreement is very good. A more demanding test is furnished by Fig. 5, where the modulated reflectivity of Shen and Zucca is shown with the results of our calculation. The theoretical curve was obtained by direct numerical calculation from the computed reflectivity, without introducing any broadening or smoothing. The similarity between the theoretical and experimental curves indicates that no spurious effects have been introduced by differentiating the calculated reflectivity. This demonstrates that our procedure is quite free from statistical fluctuations in the calculation of ϵ_2.

Note added in proof. We believe that the main source of disagreement in the magnitude of $\epsilon_2(\omega)$ (Fig. 6) between the theoretical calculation of Ref. 4 and the present paper results from the retention of a factor of 2 for spin degeneracy in the calculations of Ref. 4. This factor should not appear since each band is calculated explicitly when spin-orbit interaction is included.[23]

In considering possible adjustments of the present calculation, we were guided by two observations. First, the valence and first conduction bands seem to be well accounted for. The agreement with experimental data

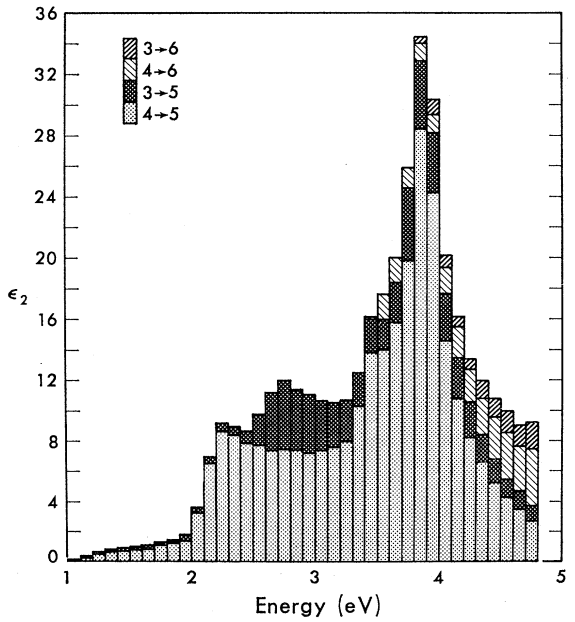

FIG. 5. Imaginary part of the dielectric function of GaSb. The total theoretical ϵ_2 is divided into contributions from interband transitions. The bands are numbered as if there were no spin-orbit interaction although spin-orbit interaction was included in the calculation.

[23] We would like to acknowledge communications with Dr. H. I. Zhang.

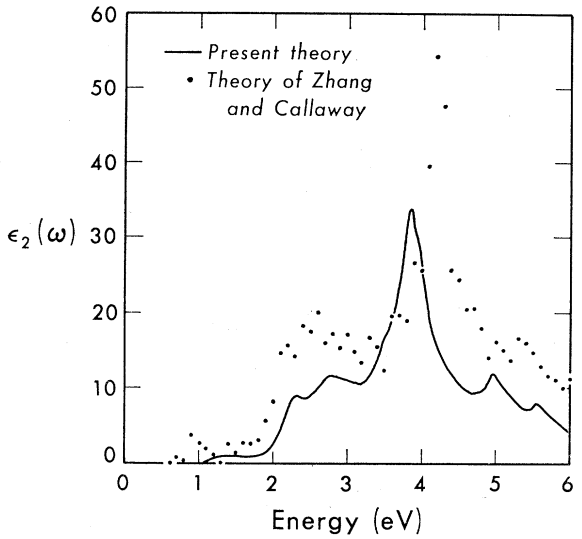

FIG. 6. Imaginary part of the dielectric function of GaSb. The solid line is given by the present theory. The points are the calculated theoretical values of Ref. 4.

is very good, not only for the reflectivity, but even for the more sensitive modulated reflectivity. Second, the structure above the main peak corresponds closely to experiment, especially that of Zucca and Shen,[22] except that all our structures are displaced about 0.4 eV down from the experiment. In particular, there are two large peaks in the derivative of the reflectivity which are generally attributed to the spin-orbit split L_3^v-L_3^c. More precisely, these are volume effects including L.[8] The lower peak shows signs of the small spin-orbit splitting of L_3^c. The theoretical splittings are in agreement with the observed data. In addition, between the main peak and these higher L peaks, some smaller structure is observed in both the experiment and theory.

In view of these successes, only a minimal adjustment in the present calculation would be desirable. One approach is to introduce as a single parameter $\alpha=m^*/m$. This would have the effect of scaling all energies by α. An $\alpha=0.93$ would bring the main peak and higher structure into agreement with experiment. The lower peaks would be moved much less and a small form factor adjustment might offset this change. It is not clear that the 0.4-eV discrepancies above 5 eV warrant the introduction of a new parameter, however.

ACKNOWLEDGMENTS

We are grateful to Professor R. Shen and R. Zucca for the use of their data prior to publication. We have profited from discussions with Professor C. Y. Fong, Mrs. Y. Tsang, and J. P. Walter.