HIGH RESOLUTION BAND STRUCTURE AND
THE $E_2$ PEAK IN Ge

James R. Chelikowsky and Marvin L. Cohen

October 1973

Prepared for the U. S. Atomic Energy Commission
under Contract 7405-ENG-48

For Reference
Not to be taken from this room
High Resolution Band Structure and the $E_2$ Peak in Ge*

James R. Chelikowsky† and Marvin L. Cohen

Department of Physics, University of California

and

Inorganic Materials Research Division, Lawrence Berkeley Laboratory

Berkeley, California 94720

Abstract

We find evidence that the $E_2$ optical peak in Ge arises from transitions in a well-defined, limited region inside the Brillouin zone. This conclusion is compatible with the recent experimental results of Aspnes. The region of interest is not on symmetry lines, but it is close to the $(3/4, 1/4, 1/4)$ special point determined by Chadi and Cohen. The calculated modulated reflectivity, density of states, and interband masses are in good agreement with experiment.

Recently Aspnes$^1$ has proposed that the $E_2$ reflectivity peak, the most prominent peak, in Ge appears to arise from a localized region in the Brillouin zone (BZ) in apparent contradiction to previous theoretical calculations.$^{2,3,4,5,6}$ By using a non-local pseudopotential scheme, we are able to determine that the interband transitions of interest arise from a specific BZ region; these conclusions are not at variance with the experimental results. Analysis of the calculated reflectivity reveals that the $E_2$ peak arises from a well defined, limited region inside the BZ which
is not along lines of high symmetry. This region lies near the special point 
\((3/4, 1/4, 1/4)\) determined by Chadi and Cohen.\(^8,^9\) These results are consistent with previous theoretical calculations and with Aspnes' suggestion that the observed structure can arise from a set of equivalent critical points. We also obtain an interband mass for the\(E_2\) region in reasonably good accord with the experimentally determined value.

In addition, our non-local pseudopotential calculation yields a derivative reflectivity spectrum and density of states in excellent agreement with experiments on modulated reflectivity, X-ray photoemission spectroscopy (XPS), and ultraviolet photoemission spectroscopy (UPS).

The band structure was calculated using the Empirical Pseudopotential Method (EPM) which has been discussed extensively elsewhere.\(^7,^10\) For the atomic pseudopotential we took a non-local pseudopotential of the form,

\[
V_{NL}(r) = V_L(r) + A_2 f(r) \rho_2
\]

where \(V_L(r)\) is the usual local atomic pseudopotential, \(f(r)\) is given by \(f(r) = \exp\left(-r^2/R^2\right)\), and \(\rho_2\) projects out the \(\ell = 2\) angular momentum component.

This non-local pseudopotential is quite similar to the one used recently by Phillips and Pandey.\(^11\) It has been noted by them, and elsewhere\(^12\) that such a non-local d-well potential is necessary to obtain agreement with both the optical reflectivity and the density of states as determined by experiment. However, unlike the Phillips-Pandey calculation we have not used a square well for \(f(r)\), but rather a gaussian well. The gaussian
well probably resembles more closely the true potential, and is computationally simpler. As can be noted in Table 1, we obtain comparably agreement with experimentally known transitions. The local form factors used were those of Phillips and Pandey with minor modification, and the gaussian well radius, $R$, (i.e. the $1/e$ value) was also chosen to coincide with their square well radius. For the well height we have used $A_2 = 0.55$ Ryd.

Once the band structure has been obtained the imaginary part of the dielectric function, $\varepsilon_2(\omega)$, is calculated using the Gilat-Raubenheimer technique. The real part of the dielectric function, $\varepsilon_1(\omega)$, can then be calculated by the Kramers-Krönig dispersion relations, and a reflectivity, $R(\omega)$ obtained.

In Figure 1 the experimental and theoretical modulated reflectivity is given for Ge, and as can be observed, the agreement is excellent. In Table 2 identification of the important reflectivity structure is tabulated. Since we have not included spin-orbit interactions in our calculations, the usual $E_1$ doublet does not appear in the theoretical reflectivity in Figure 1. We also have not included exciton effects which accentuates the experimental $E_1$ doublet. It is interesting to note that the usual $\Lambda_3 - \Lambda_1$ critical point has been effectively displaced to $L_3' - L_1$ in our calculation. Hence, no $L_3' - L_1 M_0$ critical point exists. It is possible, however, that the usual $L_3' - L_1 M_0$ critical point can be reinstated with a small change in the potentials and the experimental situation has yet to be clearly resolved.
The $E'_0$ structure near 3.3 eV comes from a $\Delta_5 - \Delta_1 M_1$ critical point. While the $\Gamma_{25}' - \Gamma_{15} M_0$ critical point occurs at this energy, it occupies a small volume and does not contribute significantly to this feature. This is the usual case in band structure calculations; however, experimentally it is possible that exciton effects could enhance the $\Gamma_{25}' - \Gamma_{15}$ transition.

In analyzing the $E_2$ peak we find that it originates from a specific region of the $\Gamma$-X-U-L plane. Figure 2 indicates the energy contours of interest in this region. This very flat plateau region has large dipole matrix elements and because it is not a point of high symmetry there are 48 equivalent regions in the full Brillouin zone making up a large volume. Further, we find no critical point along $\Sigma$, and as noted elsewhere the $X_4 - X_1$ critical point is of little consequence due to its small volume. Such a plateau feature has been noted before in zincblende compounds and Ge, where it usually, but not always, is accompanied by a $\Sigma$ critical point.

The plateau itself, consists of a nearly, if not completely, degenerate $M_1 - M_2$ pair of critical points, and while it is not a "localized" region in the sense of a critical point at a symmetry point, it is still a well-defined and limited region. The dipole matrix elements and energy difference of bands 4 and 5 are nearly constant over the entire plateau. And as will be mentioned in more detail below, the interband mass in this region is also nearly constant. Finally it has been noted that the $E_2$ peak in the $\epsilon_2(\omega)$ appears to arise from just such a combination, and Aspnes has
determined that at least one interband mass component should be negative in this region. Both of these results are compatible with our calculations.

The $E_1'$ structure in our theoretical modulated reflectivity comes from an $L_3'$ - $L_1$ critical point, and, again, no doublet occurs in the theory due to the absence of spin-orbit interactions.

In order to compare the interband masses as experimentally determined by Aspnes to our resulting band structure, we have calculated some interband masses from the following expression:

$$ \frac{m}{m_{ij}} = \frac{2\hbar^2}{m} \sum_{\ell} \left( \frac{P_{\ell}^2}{E_j - E_{i\ell}} - \frac{P_{i\ell}^2}{E_i - E_{i\ell}} \right) $$

(2)

where $m_{ij}$ is a measure of the interband mass size for the $i$th and $j$th bands, and $P_{i\ell}$ is the gradient matrix element. We have calculated $m_{45}$ for several points in the plateau region with a range of 0.09m to 0.11m, with the latter value closer to the center of the region. Our results for the interband masses are compared with the experimental results of Aspnes in Table III, and the results are in reasonably good agreement.

Finally we note a possible relationship between the plateau region and the special point $(3/4, 1/4, 1/4)$ of Chadi and Cohen, who have developed a scheme for evaluating sums over wave vector in the Brillouin zone of a periodic function. They have found that by choosing special points in $k$-space, rapid convergence of the sum can be achieved (e.g. for charge density calculations).

In particular, if we have
they have shown that the best two point approximation which can be made is

\[ f = \sum_k g(k) \]  

\[ f \approx \frac{1}{4} g(k_1) + \frac{3}{4} g(k_2) \]

where \( k_1 = (1/4, 1/4, 1/4) \) and \( k_2 = (3/4, 1/4, 1/4) \). It is interesting that such a two point \( \epsilon_2(\omega) \) would pick up a contribution to the \( E_1 \) and \( E_1' \) peaks from \( k_1 \) and a contribution to the \( E_2 \) peak from \( k_2 \). Of course, it is just these peaks which dominate the structure. This would seem to indicate such a scheme might be applicable in evaluating the sum over wave vector needed for dielectric function calculations; further investigations are under way.

In conclusion we have found a specific limited region in the Brillouin zone giving rise to the \( E_2 \) structure in the optical spectrum in accordance with the results of Aspnes. Further by using a non-local pseudopotential scheme we are able to obtain excellent agreement with the experimental reflectivity and density of states, and fairly good agreement with the measured interband masses. We have also noted the possibility of applying the Chadi-Cohen special point scheme to evaluating the dielectric function.

**Acknowledgement**

One of us (J. R. C.) expresses his gratitude to D. J. Chadi and C. Varea de Alvarez for helpful discussions on the special point scheme. Part of this work was done under the auspices of the U.S. Atomic Energy Commission.
References

* Supported, in part, by the National Science Foundation Grant GH 35688.
† Supported by a National Science Foundation Predoctoral Fellowship.
9. Calculations using special points for the chalcopyrite structures have also led to the special point $(3/4, 1/4, 1/4)$ as being a good representative point for charge density calculations. C. Varea de Alvarez and M. L. Cohen, to be published.
13. We have increased their value of $\Psi(3)$ by 0.001 Ryd.


Table Captions

Table I. Comparison of theoretical and experimental transitions for Ge. Spin-orbit interactions have been subtracted out from the experimental values.

Table II. Theoretical and experimental reflectivity structure at 50K (from Ref. 20), and their identifications, including the location in the Brillouin zone, energy and symmetry of the calculated critical points.

Table III. Comparison of the theoretical interband mass, $m_{ij}$, from Eq. (2), with the experimental values. Absolute values are tabulated, and the notation is from Ref. 1.

Figure Captions

Figure 1. A comparison of theoretical (solid line) and experimental (dotted line) modulated reflectivity for Ge. (The experimental results are from Ref. 20.)

Figure 2. Energy contours for the 4-5 transitions for the region of the Brillouin zone which contributes to the $E_2$ peak. The part of the $\Gamma$-X-U-L plane displayed is indicated by the shaded region. The contours are drawn in 0.01 eV steps. (Contours below 4.30 eV and above 4.43 eV are not included.)
<table>
<thead>
<tr>
<th>Transition</th>
<th>Experiment (eV)</th>
<th>Theory (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1' - r_{25}'$</td>
<td>$12.6 \pm 0.3^a$, $12.8 \pm 0.4^b$</td>
<td>12.56</td>
</tr>
<tr>
<td>$L_2' - r_{25}'$</td>
<td>$10.6 \pm 0.4^a$, $10.5 \pm 0.4^b$</td>
<td>10.30</td>
</tr>
<tr>
<td>$L_1' - r_{25}'$</td>
<td>$7.7 \pm 0.2^a$, $7.4 \pm 0.2^b$</td>
<td>7.52</td>
</tr>
<tr>
<td>$\Sigma_{1\text{min}}' - r_{25}'$</td>
<td>$4.5 \pm 0.2^a$, $4.5 \pm 0.3^b$</td>
<td>4.55</td>
</tr>
<tr>
<td>$L_3' - r_{25}'$</td>
<td>$1.4 \pm 0.2^c$</td>
<td>1.44</td>
</tr>
<tr>
<td>$r_{25}' - r_2'$</td>
<td>$0.98^d$</td>
<td>0.99</td>
</tr>
<tr>
<td>$r_{25}' - r_{15}$</td>
<td>$3.24^e$</td>
<td>3.25</td>
</tr>
<tr>
<td>$r_{25}' - L_1$</td>
<td>$0.87^f$</td>
<td>0.85</td>
</tr>
<tr>
<td>$r_{25}' - X_1$</td>
<td>$1.2^g$</td>
<td>1.25</td>
</tr>
<tr>
<td>$r_{25}' - L_3$</td>
<td>$4.3^c$</td>
<td>4.30</td>
</tr>
</tbody>
</table>

a) See Ref. 16 (UPS).
b) See Ref. 21 (XPS).
c) See Ref. 17.
d) See Ref. 22.
e) See Ref. 18.
f) See Ref. 19.
g) See Ref. 5.
<table>
<thead>
<tr>
<th>Reflectivity Structure (eV)</th>
<th>Associated Critical Points</th>
<th>Symmetry</th>
<th>Critical Point Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory</td>
<td>Experiment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.28</td>
<td>2.22&lt;sup&gt;a&lt;/sup&gt;</td>
<td>L&lt;sub&gt;3&lt;/sub&gt;'-L&lt;sub&gt;1&lt;/sub&gt; (0.5,0.5,0.5)</td>
<td>M&lt;sub&gt;1&lt;/sub&gt;</td>
</tr>
<tr>
<td>3.25</td>
<td>3.20</td>
<td>Δ&lt;sub&gt;5&lt;/sub&gt;-Δ&lt;sub&gt;1&lt;/sub&gt; (0.1,0.,0.)</td>
<td>M&lt;sub&gt;1&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>r&lt;sub&gt;25&lt;/sub&gt;'-r&lt;sub&gt;15&lt;/sub&gt; (0.,0.,0.)</td>
<td>M&lt;sub&gt;0&lt;/sub&gt;</td>
</tr>
<tr>
<td>4.50</td>
<td>4.49</td>
<td>Bands (4-5) Near (0.75,.25,.25)</td>
<td>M&lt;sub&gt;1&lt;/sub&gt;-M&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>5.03</td>
<td>5.01</td>
<td>Vol. (4-5) near (.7,.25,.1)</td>
<td>--</td>
</tr>
<tr>
<td>5.38</td>
<td>--</td>
<td>Δ&lt;sub&gt;5&lt;/sub&gt;-Δ&lt;sub&gt;2&lt;/sub&gt;' (.5,0.,0.)</td>
<td>M&lt;sub&gt;1&lt;/sub&gt;</td>
</tr>
<tr>
<td>5.78</td>
<td>5.65&lt;sup&gt;a&lt;/sup&gt;</td>
<td>L&lt;sub&gt;3&lt;/sub&gt;'-L&lt;sub&gt;3&lt;/sub&gt; (.5,.5,.5)</td>
<td>M&lt;sub&gt;1&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Spin-orbit splitting.
**Table III.**

<table>
<thead>
<tr>
<th>Transition</th>
<th>Mass Component (field [110])</th>
<th>Expt. Value(^a) (in (m_e))</th>
<th>Theor. Value(^b) (in (m_{ij}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_0)</td>
<td>(\mu_{hh'}, \bar{\epsilon}[1\bar{1}0])</td>
<td>0.036±0.013</td>
<td>0.022</td>
</tr>
<tr>
<td>(E_0 + \Delta_0)</td>
<td>(\mu_{so})</td>
<td>0.0269</td>
<td></td>
</tr>
<tr>
<td>(E_1)</td>
<td>(\mu_T)</td>
<td>0.045±0.004</td>
<td>0.050</td>
</tr>
<tr>
<td>(E_1 + \Delta_1)</td>
<td>(\mu_T)</td>
<td>0.042±0.005</td>
<td></td>
</tr>
<tr>
<td>(E'_0)</td>
<td>(\mu, \bar{\epsilon}[001])</td>
<td>0.034±0.005</td>
<td>0.047(^c)</td>
</tr>
<tr>
<td>(E'_0 + \Delta'_0)</td>
<td>(\mu, \bar{\epsilon}[1\bar{1}0])</td>
<td>0.048±0.009</td>
<td></td>
</tr>
<tr>
<td>(E'_0 + \Delta'_0 + \Delta_0)</td>
<td>(\mu, \bar{\epsilon}[001])</td>
<td>0.062±0.006</td>
<td></td>
</tr>
<tr>
<td>(E_2)</td>
<td>(\mu_T(?))</td>
<td>0.139±0.015</td>
<td>0.11</td>
</tr>
</tbody>
</table>

a) See Ref. 1.  
b) Spin-orbit interactions have not been included.  
c) The \(E'_0\) interband mass is from \(\Gamma_{25}'-\Gamma_{15}'\).
Fig. 1

Ge

- EXPERIMENT
- THEORY
(without spin-orbit)
Fig. 2
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.