Title
CALCULATED VALENCE BAND DENSITY OF STATES AND REFLECTIVITY FOR ZnSe

Authors
Chelikowsky, James R.
Cohen, Marvin L.

Publication Date
1973-12-01

Submitted to Physics Letters

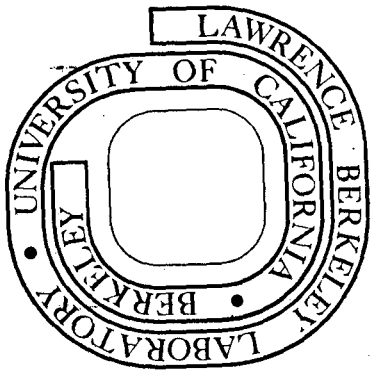
LBL-2555
Preprint

CALCULATED VALENCE BAND DENSITY OF STATES AND REFLECTIVITY FOR ZnSe

James R. Chelikowsky and Marvin L. Cohen

December 1973

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



DISCLAIMER

Calculated Valence Band Density of States and Reflectivity for ZnSe*

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

Using a non-local pseudopotential, including spin-orbit interactions, we calculate a valence band density of states for ZnSe which is in significantly better agreement with experiment than previous local pseudopotential calculations. The calculated reflectivity spectrum is also presented.

Local pseudopotential calculations do not accurately reproduce the experimental results from photoemission spectroscopy measurements.[1] However, this situation can be remedied by the inclusion of a non-local d-well pseudopotential. In such a manner we have been able to obtain excellent agreement with experiment for both the optical properties and the density of states for Ge and GaAs.[2,3] Here we extend the calculations to ZnSe. The resulting density of states has been greatly improved over local pseudopotential calculations, at least for the top three valence bands. On the other hand, the calculated reflectivity based on this model shows only moderate improvement.

In calculating the band structure of ZnSe we have used the empirical pseudopotential method (EPM).[4] This method consists of adjusting pseudopotential form factors to achieve agreement with the experimental data. In addition to the local form factors, a non-local correction of the form: $V_{NL}(r) = A_2 \exp(-r^2/R^2)\,\mathcal{P}_2$, has been included in the present calculation. A_2 is the well depth, R the well size, and $\mathcal{P}_2$ is a projection operator acting on the d-component of the wavefunction. The well depths for Zn and Se were determined by adjustment to agree with experiment. The well sizes were not so adjusted, but constrained so that $R_{Zn} + R_{Se} = 2R_{Ge}$,[2] with the relative size of R_{Zn} to R_{Se} determined by Slater's rules. Spin-orbit interactions were included in a manner similar to Saravia and Brust's calculation for Ge.[5]

In Figure 1 we compare our calculated valence band density of states with the experimental results of ultraviolet photoemission spectroscopy (UPS)[6] and x-ray photoemission spectroscopy (XPS).[7] Previous local EPM calculations[1,8] were in disagreement for the top three valence band edges by an eV or more. The non-local pseudopotential calculation has removed this discrepancy. However, the bottom valence band, which corresponds to the Se 4s states, is not in good agreement with the XPS data. In UPS the bottom band is not observed. It is not clear why our position for the bottom band is in error. OPW calculations tend to give better values than the local EPM calculations for the lowest band, and such calculations agree with our results.[6] Further, Freeouf

has recently studied the experimental reflectivity of II-VI compounds over an extended energy range by the use of synchotron radiation.[9] He observes structure in the 15-16 eV range, and notes that such structure might be associated with transitions from the group VI s-level. Our calculation agrees with this suggestion as the threshold for such a transition is 15 eV.

In Figure 2 we compare our calculated reflectivity to the experimental results of Petroff and Balkanski,[8] and Freeouf.[9] With the exception of the doublet nature of the E_2 peak, which does not appear in our calculated reflectivity, we achieve fairly good agreement. In particular, the positions of the higher energy structure have been improved over the local EPM results;[8] however, the magnitude of the peaks are not in agreement with experiment. This discrepancy was also present in the case of the local EPM calculation.

References

* Supported in part by National Science Foundation Grant GH 35688 and the the U. S. Atomic Energy Commission.

1. J. R. Chelikowsky, D. J. Chadi, and M. L. Cohen, Phys. Rev. B8, 2786 (1973).

2. J. R. Chelikowsky and M. L. Cohen, Phys. Rev. Lett. (in press).

3. J. R. Chelikowsky and M. L. Cohen (to be published).

4. M. L. Cohen and V. Heine, Solid State Physics 24, 37 (1970).

5. L. R. Saravia and David Brust, Phys. Rev. 176, 915 (1968).

6. D. E. Eastman, W. D. Grobman, J. L. Freeouf, and M. Erbudak, Phys. Rev. B (in press).

7. L. Ley, R. Pollak, F. R. McFeely, S. P. Kowalczyck, and D. A. Shirley, Phys. Rev. B (in press).

8. John P. Walter, M. L. Cohen, Y. Petroff, and M. Balkanski, Phys. Rev. B1, 2661 (1970).

9. John L. Freeouf, Phys. Rev. B7, 3810 (1973).

Figure Captions

Figure 1. X-ray photoemission spectra from Ref. 7 (dotted line) and ultraviolet photoemission spectra from Ref. 6 (dashed line) in arbitrary units compared to the calculated density of states (solid line). There appears to be a uniform shift between the XPS and UPS data of approximately 0.5 eV. The UPS results appear to be in better agreement with the calculated results. The Zn 3d core states, which occur at approximately 9 eV below the top of the valence band, have been subtracted out of the experimental spectra.

Figure 2. Measured reflectivity spectra from Ref. 8 (dashed line) and Ref. 9 (dotted line) compared to the calculated reflectivity spectra (solid line).

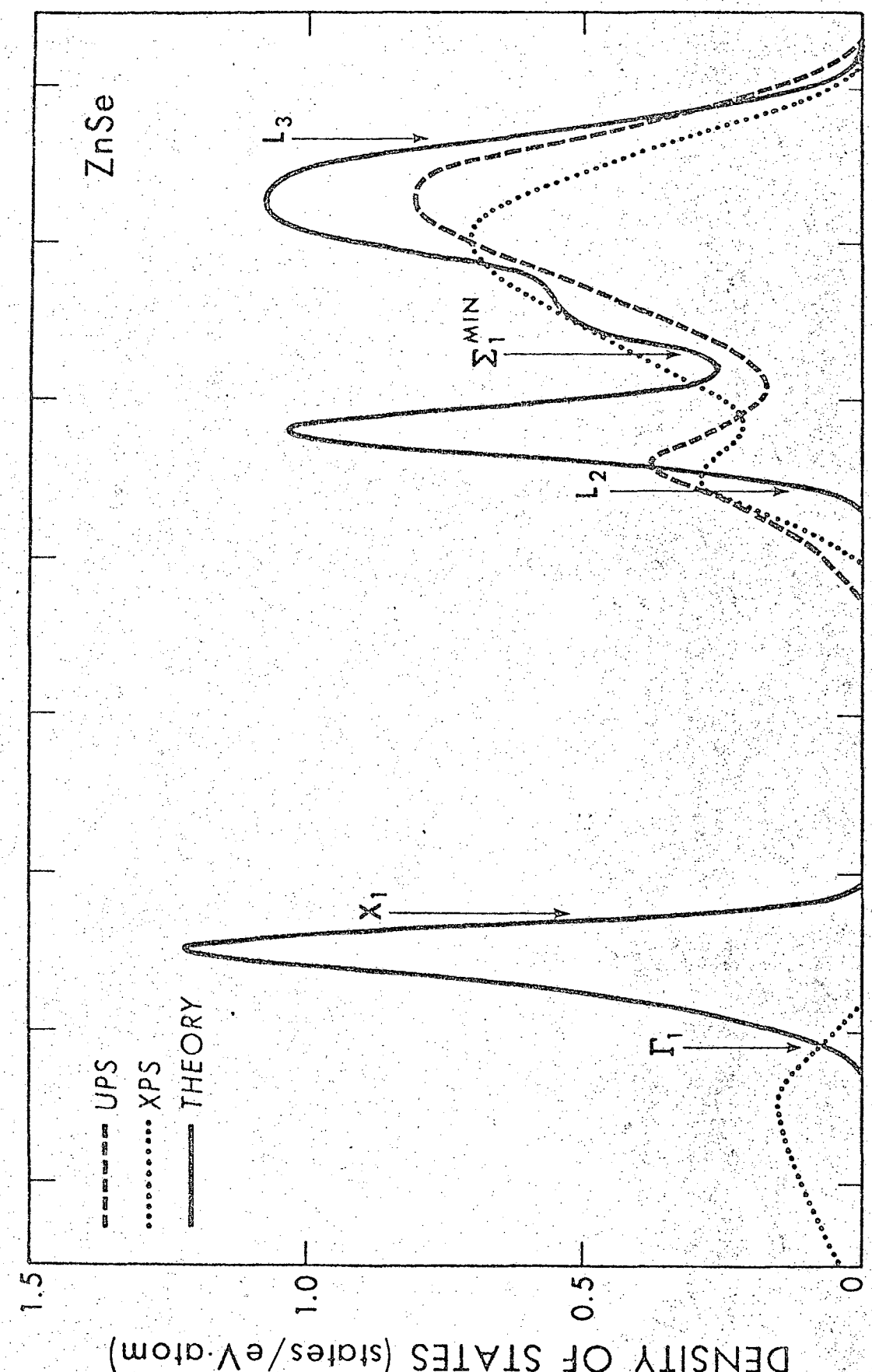

ZnSe
UPS
XPS
THEORY
Γ_1
X_1
Σ_1^{MIN}
L_3
L_2
DENSITY OF STATES (states/eV·atom)
ENERGY (eV)
0
0.5
1.0
1.5
0
2
4
6
8
10
12
14

Figure 1

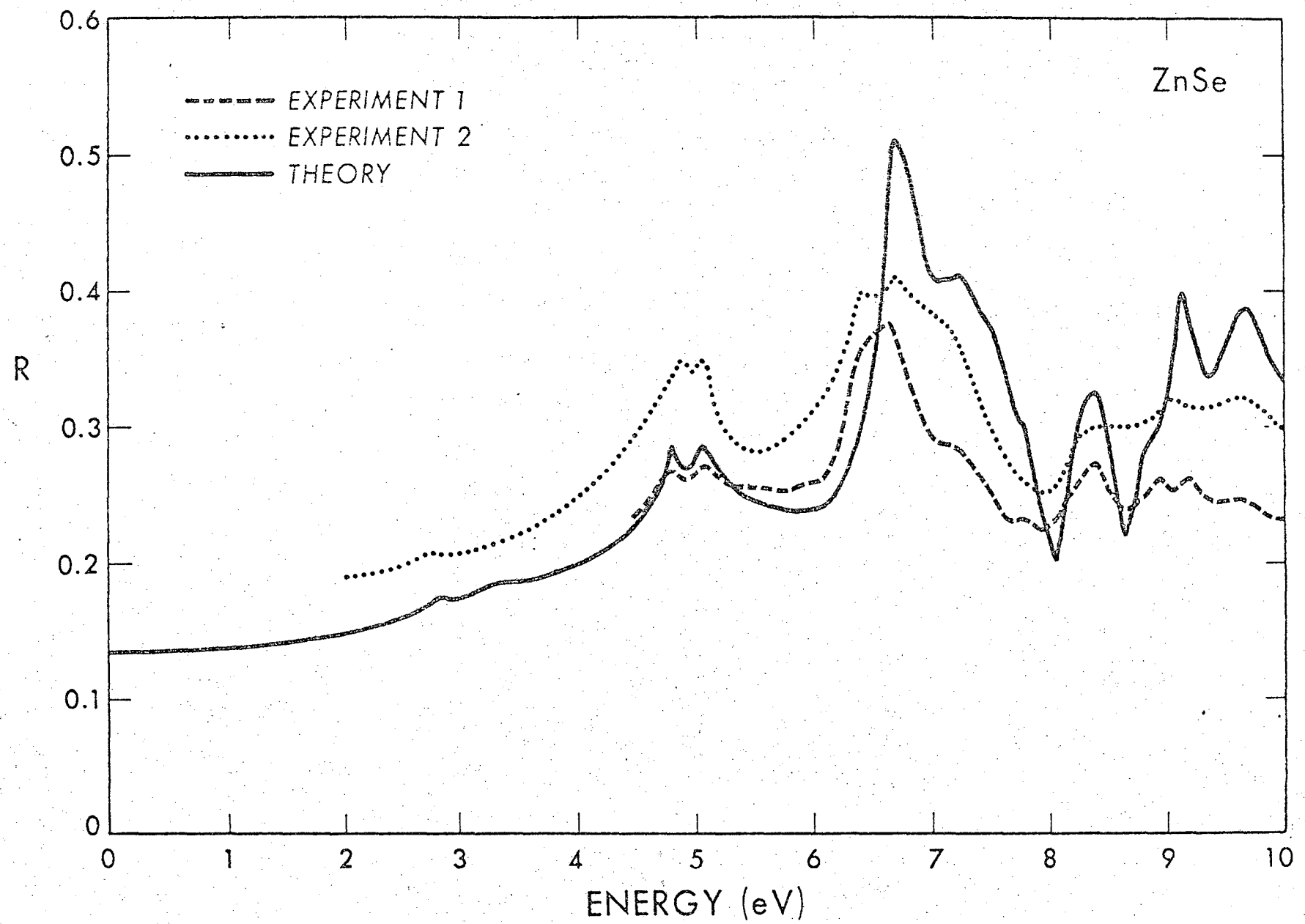

ZnSe
EXPERIMENT 1
EXPERIMENT 2
THEORY
R
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
6
7
8
9
10
ENERGY (eV)

Figure 2

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720