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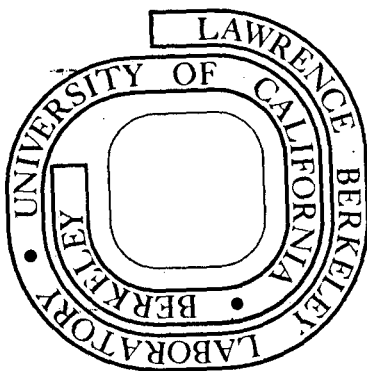
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Calculated Valence Band Density of States and Reflectivity for ZnSe\*

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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.<sup>1</sup> 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.<sup>2,3</sup> 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).<sup>4</sup> 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  $R_{Zn} + R_{Se} = 2R_{Ge}$ ,<sup>2</sup>

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.<sup>5</sup>

In Figure 1 we compare our calculated valence band density of states with the experimental results of ultraviolet photoemission

spectroscopy (UPS)<sup>6</sup> and x-ray photoemission spectroscopy (XPS).<sup>7</sup>

Previous local EPM calculations<sup>1,8</sup> 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.<sup>6</sup> Further, Freeouf

has recently studied the experimental reflectivity of II-VI compounds over an extended energy range by the use of synchrotron radiation.<sup>9</sup> 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,<sup>8</sup> and Freeouf.<sup>9</sup> 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;<sup>8</sup> 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.
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### 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).



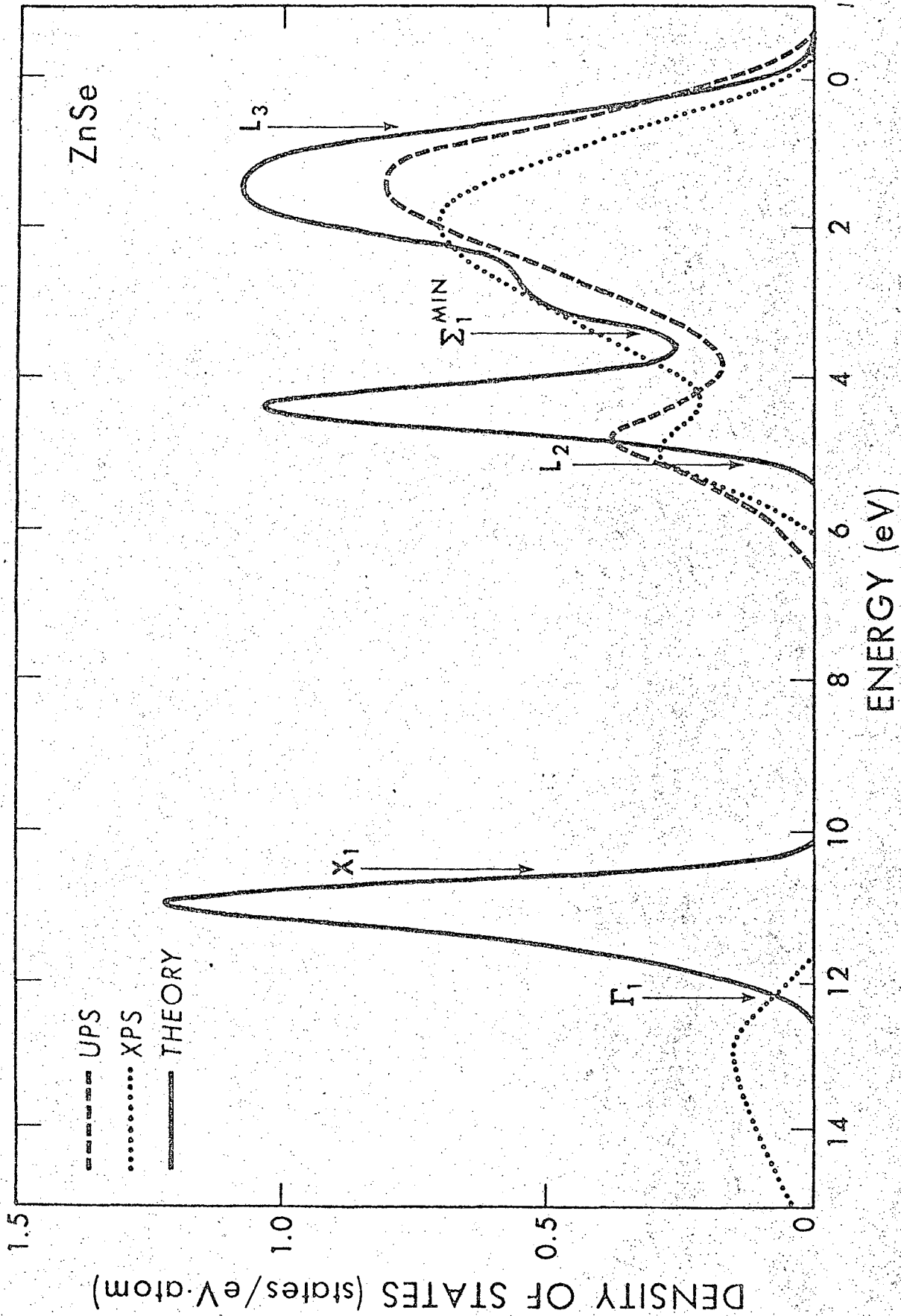


Figure 1

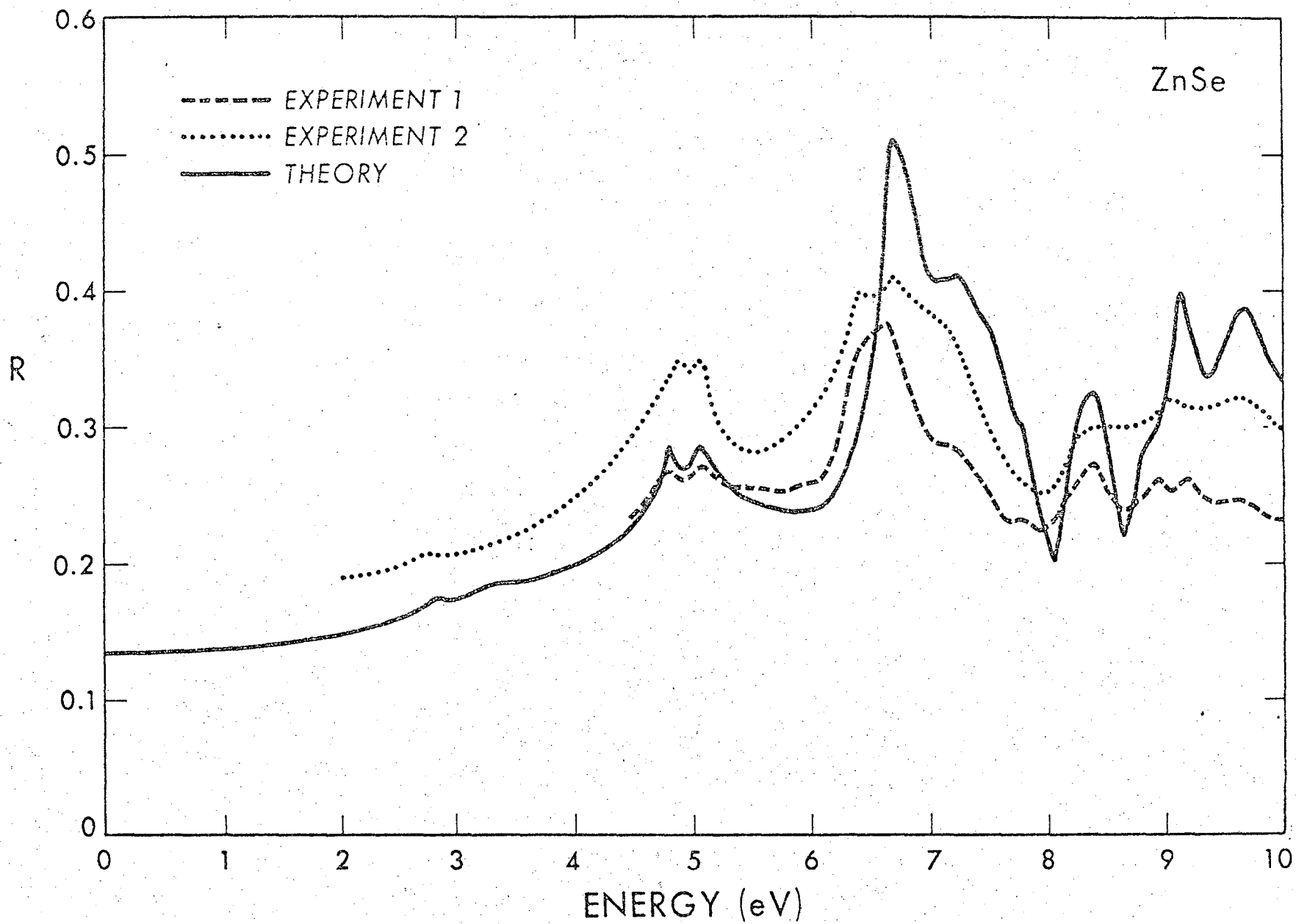


Figure 2

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