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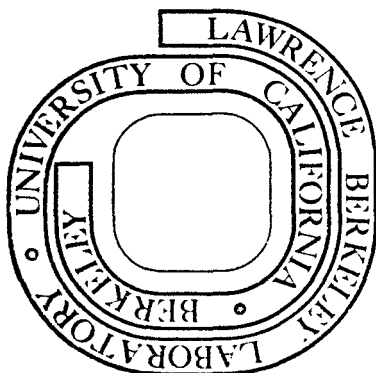
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Calculated Valence Band Densities of States and Photoemission
Spectra of Diamond and Zincblende Semiconductors. *

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Abstract

Density of states calculations are presented based on band structures computed using the Empirical Pseudopotential Method. Data from recent XPS (x-ray photoemission spectra) and UPS (ultraviolet photoemission spectra) are used to obtain the theoretical parameters. It was necessary to include a nonlocal pseudopotential to obtain consistency with experiment. Results for the density of states including critical point assignments and band structures are given for Si, Ge, GaAs, InSb, GaP, ZnSe and CdTe.

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I. Introduction

With the advent of high resolution photoemission spectroscopy, i. e. x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS), detailed information is now available^{1,2,3} about the lowest lying valence bands in semiconductors. In this paper we identify the structure in those spectra and associate it with structure in the valence band density of states. To do this we have calculated the band structures and density of states for Si, Ge, GaAs, GaP, InSb, ZnSe, and CdTe using the Empirical Pseudopotential Method (EPM).^{4,5}

The EPM uses experimental data to fix the form factors of the crystalline potential. In the past, reflectivity data was the main source of experimental input. It was found that a completely local potential was sufficient to explain most of the reflectivity data. On purely theoretical grounds the pseudopotential should be non-local and energy dependent, but local approximations suffice for a limited energy range. This is the situation for the reflectivity case where the predominant structure results from transitions between the top valence and bottom conduction bands. When we extend the early calculations to lower energies/comparisons with XPS and UPS data show discrepancies. In addition, reflectivity assignments fit direct transitions. When XPS or UPS data is used, it is possible to fix indirect splittings. It was found that even regions of the second highest valence bands were in disagreement with experiment. A non-local pseudopotential scheme completely removes the discrepancies above. In this paper we take the simplest approach to get the lowest order corrections by allowing the electron

mass to vary, i. e. $m \rightarrow m^*$. A more traditional (and theoretically pleasing) approach⁴ would be to include a specific non-local potential (e. g. for d-waves), but the results are similar. We, therefore, have chosen the former scheme because it is simple.

We begin by calculating the density of states with a local potential and then fit the non-local parameter, i. e. m^* and the form factors of the potential by comparing the density of states with XPS and UPS data. One of the most striking features of the XPS and UPS spectra is that they both mimic the valence band density of states. In addition, the agreement between the two (XPS and UPS) is excellent. Considering that the bulk penetration of electrons is different in the two cases this adds support to the idea that both XPS and UPS measure bulk properties.

After the density of states fits are obtained (reflectivity data is also used as a constraint), a critical point (cp) analysis is done. The sharp structure is identified with the M_0, M_1, M_2, M_3 cp's⁴ in the energy band structure. The band structure itself is given for each crystal studied.

The overall agreement is good and the major discrepancies between experiment and the local EPM calculations have been removed especially for the highest bands. The lowest band is the least reliable; this stems partially from the approximate manner in which we have included non-local effects.

In the text comparison is made between the present calculation using the non-local potential, experimental results and the original calculations using the EPM by Cohen and Bergstresser⁵ (CB). More recent EPM calculations since CB have been done which give better agreement with experi-

mental reflectivity spectra. However, in these calculations again very little attention is given to fitting the valence band densities of states. Despite this, the adjustment to fit optical data sometimes yielded a band structure which gave a density of states spectra closer to the XPS value. We have not, however, included these results here, as it is more straightforward and simpler to use the CB values since this reference contains all the crystals of interest and the form factors are not too different from the more recent work.

II. Methods of Calculation

The EPM involves adjusting pseudopotential form factors to achieve good agreement with the experimental results. These form factors are then used to calculate the electronic energy bands on a fine mesh of points throughout the Brillouin zone.⁴

In applying the EPM to obtain the electronic band structures, we have used the pseudopotential Hamiltonian

$$H = -\frac{\hbar^2}{2m^*} \nabla^2 + V(\underline{r}) \quad (1)$$

where m^* is an effective mass and $V(\underline{r})$ is a weak pseudopotential which is taken to be a superposition of spherical atomic pseudopotentials.

The potential $V(\underline{r})$ is then expanded in reciprocal lattice vectors, and for convenience expressed in terms of a symmetric and antisymmetric part

$$V(\underline{r}) = \sum_{\underline{G}} [V^S(\underline{G}) \cos(\underline{G} \cdot \underline{r}) + iV^A(\underline{G}) \sin(\underline{G} \cdot \underline{r})] \exp(-i\underline{G} \cdot \underline{r}) \quad (2)$$

where $\underline{r} = \frac{a}{8} (1, 1, 1)$, "a" being the lattice constant. (For diamond structure compounds, the antisymmetric form factors, $V^A(\underline{G})$ are zero.) The above series usually converges rapidly enough so that only three form factors are needed for each atom.

As a starting point for these calculations the CB form factors were used.⁵ Adjustments were then made in these form factors to obtain a good fit to the experimentally determined density of states. The principal optical transitions at Γ , X, L and Σ were constrained to remain near their original values.

One modification of the usual procedure used in EPM calculations was made. As is well-known, the pseudopotential appearing in (1) is non-local. However, the "local" approach can be simply modified to take this fact into account in an approximate way. It has been noted,^{2,4} that the lowest order correction to this inherent non-local behavior is to replace the free electron mass in the Hamiltonian by an effective mass, m^* . Such a procedure has been used before in EPM calculations especially when fits to orthogonalized plane wave results⁶ are needed.

This approach is required here because the valence bands of interest span an energy range ~ 15 eV over which it was found that the pseudopotential could not be treated by purely local methods. Local approximations to the potential were sufficient for reflectivity fits since the transitions involved

were direct, of low energy and mainly between the top valence and bottom conduction bands. When indirect interband splittings were known, non-local adjustments were necessary.⁷ This is similar to what we find for photoemission where the measured density of states gives us information about non-direct splittings.

Spin-orbit interactions were included for InSb, ZnSe and CdTe. Here the spin-orbit splittings are comparable to the experimental resolution. The method of calculation used was that due to Weisz⁸ as modified by Bloom and Bergstresser.⁹ In this procedure two parameters are used to characterize the spin-orbit coupling.¹⁰ The metallic spin-orbit parameter is varied until one obtains the experimentally known splittings, while the non-metallic parameter is constrained to a fixed ratio between the two parameters. This ratio is equal to that of the ratio of the spin-orbit interaction for the free atoms as calculated by Herman and Skillman.¹¹ The resulting values for the metallic spin-orbit parameters for ZnSe, InSb and CdTe are 0.0006, 0.0019, and 0.0013 respectively.

Once the band structure has been obtained, the density of states, $N(E)$, may be calculated from

$$N(E) = \frac{1}{N N_a} \sum_{\vec{k}} \sum_{n,\sigma} \delta(E - E_{n,\sigma}(\vec{k})) \quad (3)$$

where N is the number of primitive cells, N_a is the number of atoms in the primitive cell, and $N(E)$ is normalized to the number of states per atom.

Eq. (3) was evaluated by using the Gilat-Raubenheimer technique.¹² The energy derivatives required by this technique were obtained by using $\vec{k} \cdot \vec{p}$

perturbation theory. A grid of 308 points in the irreducible Brillouin zone was used in the calculation.

As in the case of analyzing optical reflectivity spectra, one can identify critical points in the density of states. These points determine the regions of the Brillouin zone responsible for the structure found in the density of states. By observing the relationship of critical point locations in broadened and unbroadened density of states calculations, it is possible to obtain values for the actual positions of the critical points from experimental data.^{3,12}

The resulting form factors, effective mass parameters, and lattice constants used in the calculations are listed in Table I.

III. Results

In Figs. 1-7 the calculated densities of states are compared with the experimental results of XPS.^{1,2,12} The band structures are also presented for each compound. While in Tables II-VIII, the resulting values for various characteristic features in the density of states are listed, and compared with the results of previously calculated form factors from optical data.⁵ (For these calculations the matrix size was larger than in the CB case, i. e. $E_1 = 9$ rather than the CB value $E_1 = 7$; this gives some slight shifts in the energies.) Tables II-VIII also contain the experimental results from both XPS^{1,2,12} and UPS.^{3,13} All energy positions are measured relative to the top of the valence band as shown in the figures.

When comparing the calculated density of states using a local pseudopotential (CB) with XPS and UPS data it was found that several bands were in

error by as much as 0.5 to 2.0 eV. The largest error is for the lowest lying valence bands. Early workers recognized that the lower valence bands were not expected to be accurate since only interband transitions between the top valence and bottom conduction bands were used in the fitting procedure. As a result they did not publish the values or band structure curves for these lower bands. We have computed these bands using the form factors given in the early papers, and we have extended the energy range in this way.

The addition of an effective mass parameter brings the calculated bands closer to experiment. This is not always the case for the lowest valence band, because our method is approximate and is designed to give the first band (especially near (0,0,0)) a low energy value. A full non-local potential which accounts for d-states in the core should work better, but it is a bit more complex. The effective mass approach does, however, remove all the major discrepancies for the higher bands. In particular, the Σ_1^{min} feature (which is sharp in UPS data) has been improved considerably.

The resulting densities of states are discussed below compound by compound, and critical point identifications are noted in parentheses where unambiguous determination is possible.

Silicon (Fig. 1, Table II)

In the case of Si (only) the original CB form factors were used, without an effective mass, to calculate the density of states. This was done because the resulting density of states agreed quite satisfactorily with the experimental results of both XPS and UPS (see Table II).

The threshold of the valence band contributions to the density of states

for Si is -12.6 eV below the top of the valence band, and occurs at $\Gamma_1(M_0)$. The first peak at -10.2 eV is from $L_2(M_1)$. The contributions from the lowest band cease at -8.15 eV at $W_1(M_3)$, while the minimum of the second band occurs at -8.3 eV at $X_1(M_0)$. The large peak at -7.2 eV comes from $L_1(M_2)$. Because of the rather sharp rise of the second valence band in the energy range from -7.2 eV to -4.5 eV there is a rather sharp drop in the density of states from the L_1 peak. The onset of the third band occurs at -4.5 eV near K along Σ , thus the notation Σ_1^{\min} . The peak near -4.1 eV arises from contributions near Σ_1^{\min} and $W_2(M_1)$ at -4.0 eV. The peak at -2.8 eV is due to $X_4(M_2)$. Finally the shoulder at -1.1 eV is from $L_3(M_2)$.

Germanium (Fig. 2, Table III)

The valence band contribution to the density of states for Ge begins at -13.3 eV below the top of the valence band. This point occurs at $\Gamma_1(M_0)$, while the peak at -11.0 eV is due to $L_2(M_1)$. The contributions from the first band terminates at -9.05 eV at $W_1(M_3)$, and the minimum of the second band occurs at -9.15 eV at $X_1(M_0)$. The sharp peak at -7.8 eV arises from $L_1(M_2)$. Again there is a sharp drop in the density of states from -7.8 eV to -4.4 eV where the threshold of the third band occurs at Σ_1^{\min} . The peak near -4.0 eV comes from the minimum along with contributions from $W_2(M_1)$. The peak at -3.0 eV is due to $X_4(M_2)$. Finally the shoulder at -1.2 eV comes from $L_3(M_2)$.

From Table III, one notes that the comparison with both UPS and XPS experimental results is quite satisfactory. A considerable improvement has been made from the CB results. Further the discrepancy men-

tioned by Grobman and Eastman³ for Σ_1^{\min} , namely that the previous EPM calculation,⁵ and other band structure calculations¹⁵ give a value too close to the top of the valence band, has been removed. The calculated value of -4.4 eV is quite close to the UPS and XPS value of -4.5 eV. The agreement between theory and experiment would even be better if spin-orbit were included. The agreement with experiment for the L_2 , and Γ_1 features has not improved significantly from the CB results.

Gallium Arsenide (Fig. 3, Table IV)

The threshold of the density of states is at -13.8 eV at $\Gamma_1(M_0)$. The shoulder at -12.1 eV arises from $L_1(M_1)$. The main peak at -11.4 eV comes from the entire square face of the zone which turns out to be a surface of nearly constant energy (e.g. the energy change from X_1 to W_4 is less than 0.05 eV). Unlike the case of Ge there is a 4.5 eV gap between the two lowest valence bands. The gap extends from -11.3 eV to -6.8 eV and can be associated with the fact that the antisymmetric form factors, $V^A(G)$, are no longer zero as in the case of Ge or Si. The minimum of the second band occurs at $X_3(M_0)$. Contributing to the sharp rise, and to the large peak at -6.5 eV are critical points at -6.7 eV and -6.6 eV arising from $L_1(M_1)$ and $W_1(M_1)$ respectively. Just as in the case of Ge, there is a sharp drop near the main peak; this drop continues until the minimum of the third valence band occurring at Σ_1^{\min} at -3.9 eV is reached. This, along with W_2 at -3.5 eV, causes the sharp rise at the Σ_1^{\min} edge. This fourth band has a minimum at $W_3(M_0)$ which leads to the gradual rise to the $X_5(M_2)$ peak at -2.5 eV. The shoulder at -0.9 eV is from $L_3(M_2)$.

Table IV shows that the agreement of the calculated energies with experiment has improved considerably from the CB results. The discrepancy noted by Grobman and Eastman³ for Σ_1^{\min} has again been removed and would be even smaller if spin-orbit effects were included.

Gallium Phosphide (Fig. 4, Table V)

The calculated density of states for GaP is nearly identical to that of GaAs. The threshold occurs at -13.6 eV $\Gamma_1(M_0)$, while the shoulder at -11.8 eV corresponds to $L_1(M_1)$. As in GaAs the square face of the Brillouin zone causes the huge peak at -10.9 eV. There is a 4eV gap which extends from -10.9 eV to -6.9 eV between the lowest valence band and the next higher band. The minimum of the second band is at $X_3(M_0)$ which occurs at -6.9 eV. The sharp rise near the main peak at -6.5 eV comes from $L_1(M_0)$ at -6.7 eV and W_1 at -6.6 eV. The contribution of the third band at Σ_1^{\min} starting at -4.1 eV causes the sharp rise in the density of states; $W_2(M_1)$ at -3.7 eV also adds to the rise. The threshold of the fourth band occurs at $W_3(M_0)$ at -3.0 eV and this starts the gradual rise to the $X_5(M_2)$ peak at -2.5 eV. The shoulder at -1.0 eV is from $L_3(M_2)$.

There is good agreement between experiment and the calculated values for the top three bands. There has been a considerable improvement over the CB results for the W_1 and X_3 states. For Σ_1^{\min} the change was smaller. This is probably due to the fact that GaP is an indirect semiconductor and the indirect levels were fit roughly to the correct values by Cohen and Bergstresser when they considered the existing optical data.

Zinc Selenide (Fig. 5, Table VI)

Since spin-orbit coupling was included in the following densities of states calculations, the degeneracy of the bands, in certain directions can be removed. Hence, the bands will be labeled 1 through 8 with 1 being the lowest valence band and 8/the top valence band. To facilitate comparisons with Si, Ge, GaP and GaAs the bands are labeled using non-spin-orbit notation.

The lowest two bands (1,2) are s-like, thus spin-orbit interactions can be neglected. The minimum of the density of states occurs at $\Gamma_1(M_0)$ at -15.8 eV. The shoulder at -14.6 eV is due to $L_1(M_2)$ while the large peak at -14.2 eV is again due to the constant energy surface of the square face of the Brillouin zone. The gap to the next higher band found in zincblende extends from -14.2 eV to -5.9 eV. At -5.9 eV bands (3,4) start to contribute at $L_1(M_0)$. Interestingly enough, X_3 is not the minimum here as was the case in GaP or GaAs. Since L_1 is lower than X_3 , the large peak at -5.4 eV comes from $X_3(M_1)$ at -5.8 eV and W_1 which is split by the spin-orbit interaction into two peaks: one at -5.3 eV, the other at -5.0 eV. The minimum of band 5 occurs at Σ_1^{\min} at -3.8 eV. The doublet peaks at -3.4 eV and -3.2 eV are caused by the splitting of bands (5,6) at W_2 , and the sharp rise at -2.7 eV is from the onset of bands (7,8) at $W_3(M_0)$. The large peak at -2.1 eV is from bands (5,6) at $X_5(M_2)$, while the shoulder at -0.9 eV is from bands (5,6) at $L_3(M_3)$. The spin-orbit splitting here causes another shoulder at -0.7 from bands (7,8) at $L_3(M_3)$.

The agreement as indicated in Table VI is satisfactory except for the lowest band. Again there is marked improvement over the CB results.

Indium Antimonide (Fig. 6, Table VII)

In InSb the spin-orbit coupling was included. The threshold for the lowest band occurs at -11.3 eV at $\Gamma_1(M_0)$, while the shoulder occurring at -10.0 eV is from $L_1(M_1)$. The sharp peak at -9.5 eV comes from the square face of the Brillouin zone as in the other zincblende compounds. Again a gap appears between the two lowest valence bands. It begins at -9.4 eV and terminates at $X_3(M_0)$ at -6.2 eV. Unlike the other calculated densities of states, W_1 lies between X_3 and L_1 . At W_1 spin-orbit interactions split bands 5 and 6 by about 0.2 eV. Both of these points occurring at -6.0 eV and -5.8 eV contribute to the peak at -5.7 eV. $L_1(M_2)$ occurs at -5.7 eV at the height of the peak. Band 5 has a threshold at -3.2 eV at Σ_1^{\min} . The peaks at -3.1 eV and -2.8 eV are from the spin-orbit split bands at W_2 (bands 5 and 6). The small peak at -2.4 eV is from bands (7, 8) at $W_3(M_0)$ and $X_5(M_2)$ bands (5, 6). The peak at -2.1 eV is from bands (7, 8) at $X_5(M_2)$, while the shoulder at -1.2 eV is due to $L_3(M_3)$ from bands (5, 6).

The comparisons with experimental results found in Table VII are very good. Even the lowest band agrees with the experimental results. It is, perhaps, noteworthy that the d-states lie well below the lowest valence band. XPS data indicates the In 4d level lies about 17 eV below the top of the valence band.

Cadmium Telluride (Fig. 7, Table VIII)

Spin-orbit interactions were again included in the calculations for CdTe. The threshold of the lowest band is at -11.8 eV at $\Gamma_1(M_0)$. The two peaks in the lowest band at -11.0 eV and -10.6 eV are caused by $L_1(M_2)$ and

by the nearly constant energy surface of the square face of the Brillouin zone, respectively. The gap between the lowest band and the next lowest band begins at -10.6 eV and terminates at -4.6 eV at $X_3(M_0)$. The spin-orbit splitting between bands 3 and 4 at W_1 causes the doublet peaks at -4.3 eV and -4.0 eV. At -4.4 eV, $L_1(M_1)$ adds to the height of the first peak. The minimum of band 5 again occurs at Σ_1^{min} . This causes the sharp rise at -2.7 eV. Spin-orbit splitting between bands 5 and 6 at W_2 causes the peaks at -2.4 eV and -2.0 eV. The peak at -1.8 eV is due to the coincidence of $W_3(M_0)$ from bands (7,8) and $X_5(M_2)$ from bands (5,6). The peak at -1.5 eV is due to $X_5(M_2)$ from bands (7,8). Finally the shoulder at -1.0 eV is due to bands (5,6) at $L_3(M_3)$.

The comparison with experiment is listed in Table VIII. The overall agreement is satisfactory, although the lowest band is in poor agreement with experiment.

IV. Discussion of the Results

One can observe some interesting trends by examining the isoelectric series of Ge, GaAs, and ZnSe. The most obvious change from Ge to GaAs is that a gap appears between the first two valence bands. As previously noted² this is due to the localization of electrons in the first band around the strong As ion,¹⁵ and can be related to the antisymmetric form factors $V^A(G)$. This "antisymmetric gap" may also be related to the ionicity.¹⁷ One notes that the gap nearly doubles in size from the 4.5 eV value in GaAs to 8.2 eV in ZnSe which is more ionic.

Another trend observed in the calculated density of states is that the widths of the various peaks decrease as the compound becomes more ionic. For example, the width of the lowest band is 4.1 eV in Ge, 2.4 eV in GaAs, and 1.7 eV in ZnSe. The width of the top three bands also decreases. In Ge the width is 9.1 eV, in GaAs 6.8 eV and in ZnSe 6.0 eV.

The trends in going from InSb to CdTe follow the trends in going from GaAs to ZnSe. Namely, the "antisymmetric gap" for InSb is 3.3 eV, while the gap is 6.0 eV for CdTe. Finally, the width of the lowest band for InSb and CdTe is 1.9 eV and 1.2 eV respectively, and the top three bands also contract: 6.0 eV for InSb, and 4.6 eV for CdTe.

In summary, it has been demonstrated that the EPM, with the addition of an effective mass, can adequately reproduce the experimentally determined density of states for at least the top three valence bands. In addition, complete critical point analysis has been given, and the experimental structure identified.

Acknowledgements

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References

1. L. Ley, S. Kowalczyk, R. Pollak, and D. A. Shirley, Phys. Rev. Letters 29, 1088 (1972).
2. R. Pollak, L. Ley, S. Kowalczyk, D. A. Shirley, J. D. Joannopoulos,

- D. J. Chadi, and M. L. Cohen, Phys. Rev. Letters 29, 1103 (1972).
3. W. D. Grobman and D. E. Eastman, Phys. Rev. Letters 29, 1508 (1972).
4. M. L. Cohen and V. Heine, Solid State Physics 24, 37 (1970).
5. M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966);
referred to here as CB.
6. F. Herman, et al. in Proceedings of the International Conference of II-VI Semiconducting Compounds, Brown University, 1967 (Benjamin, New York, 1967).
7. Carmen Varea de Alvarez, J. P. Walter, Marvin L. Cohen, J. Stokes,
and Y. R. Shen, Phys. Rev. B6, 1412 (1972).
8. G. Weisz, Phys. Rev. 149, 504 (1966).
9. S. Bloom and T. K. Bergstresser, Solid State Comm. 6, 465 (1968).
10. J. P. Walter, M. L. Cohen, Y. Petroff and M. Balkanski, Phys. Rev. B1, 2661 (1970).
11. F. Herman and S. Skillman, Atomic structure calculations, (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).
12. G. Gilat and L. J. Raubenheimer, Phys. Rev. 144, 390 (1966).
13. L. Ley, R. Pollak, S. Kowalczyk, and D. Shirley, to be published.
14. W. D. Grobman and D. E. Eastman, to be published.
15. See, for example, D. J. Stukel, T. C. Collins, and R. N. Euwema, in "Electronic density of states," Proceedings of the Third International Materials Research Symposium, Gaithersburg, Maryland, 1969, edited by L. H. Bennett, National Bureau of Standards Special Publication No. 323 (U. S. GPO, Washington, D. C., 1971).

16. J. P. Walter and M. L. Cohen, Phys. Rev. B4, 1877 (1971).
17. W. D. Grobman, D. E. Eastman, and M. L. Cohen, to be published.

Figure Captions

Fig. 1. X-ray photoemission spectra, density of states, and band structure for Si. The top figure shows the corrected experimental spectra from the XPS work of R. Pollak, L. Ley, S. Kowalczyk and D. A. Shirley, Phys. Rev. Letters 29, 1088 (1972); Phys. Rev. Letters 29, 1103 (1972), and to be published. The middle figure is the EPM calculated density of states. To facilitate comparison with experiment a broadened density of states is indicated by the dashed line. The bottom figure is the EPM calculated band structure.

Fig. 2. X-ray photoemission spectra, density of states and band structure of Ge. See Fig. 1.

Fig. 3. X-ray photoemission spectra, density of states and band structure of GaAs. See Fig. 1.

Fig. 4. X-ray photoemission spectra, density of states and band structure for GaP. See Fig. 1.

Fig. 5. X-ray photoemission spectra, density of states, and band structure of ZnSe. The Zn 3d states have been subtracted out, with the peak position indicated by the solid line. See Fig. 1.

Fig. 6. X-ray photoemission spectra, density of states and band structure of InSb. See Fig. 1.

Fig. 7. X-ray photoemission spectra, density of states and band structure of CdTe. See Fig. 1.

Table Captions

Table I. Form factors (in Ry), effective mass parameter, and lattice constants (in Å).

Table II. Energies (in eV) of characteristic features in the valence band of Si (measured relative to the top of the valence band). The theoretical values are from Cohen and Bergstresser, Phys. Rev. 141, 789 (1966). The XPS values are taken from L. Ley, S. Kowalczyk, R. Pollak, and D. A. Shirley, Phys. Rev. Letters 29, 1088 (1972); Phys. Rev. Letters 29, 1103 (1972), and to be published. The UPS values are from W. D. Grobman and D. E. Eastman, Phys. Rev. Letters 29, 1508 (1972), and to be published.

Table III. Energies (in eV) of characteristic features in the valence band of Ge (measured relative to the top of the valence band). For a, b, c, see Table II.

Table IV. Energies (in eV) of characteristic features in the valence band of GaAs (measured relative to the top of the valence band). For a, b, c, see Table II.

Table V. Energies (in eV) of characteristic features in the valence band of GaP (measured relative to the top of the valence band). For a, b, c, see Table II.

Table VI. Energies (in eV) of characteristic features in the valence band of ZnSe (measured relative to the top of the valence band). For a, b, c, see Table II.

Table VII. Energies (in eV) of the characteristic features in the valence band of InSb (measured relative to the top of the valence band). For a, b, c,

see Table II.

Table VIII. Energies (in eV) of the characteristic features in the valence band of CdTe (measured relative to the top of the valence band). For a, b, c, see Table II.

Table I.

	$V^S(3)$	$V^5(8)$	$V^5(11)$	$V^A(3)$	$V^A(4)$	$V^A(11)$	m/m*	a
Si	-.211	.040	.080	-	-	-	-	5.43
Ge	-.269	.038	.035	-	-	-	1.089	5.65
GaAs	-.252	.000	.080	.068	.066	.012	1.138	5.64
GaP	-.249	.017	.083	.081	.055	.003	1.075	5.45
ZnSe	-.261	-.011	.113	.151	.130	.016	1.291	5.65
InSb	-.250	.010	.044	.049	.038	.010	1.192	6.47
CdTe	-.245	-.015	.073	.089	.084	.006	1.228	6.48

Table II.

	Theory	Experiment	
		UPS	XPS
Si			
$L_{3'}$	- 1.1	-	-
X_4	- 2.8	-	- 2.5 ± 0.3
W_2	- 4.0	-	- 3.9 ± 0.2
Σ_1^{\min}	- 4.5	- 4.7 ± 0.2	- 4.7 ± 0.3
L_1	- 7.2	- 6.4 ± 0.4	- 6.8 ± 0.2
W_1	- 8.1	-	- 8.1 ± 0.3
$L_{2'}$	-10.2	-	- 9.3 ± 0.4
Γ_1	-12.6	-12.4 ± 0.6	-12.5 ± 0.6

Table III.

Ge	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L ₃	- 1.1	- 1.2	- 1.1 ± 0.2	-
X ₄	- 2.4	- 3.0	-	- 2.7 ± 0.3
W ₂	- 3.3	- 4.0	-	- 3.9 ± 0.2
Σ ₁ ^{min}	- 3.8	- 4.4	- 4.5 ± 0.2	- 4.5 ± 0.3
L ₁	- 6.9	- 7.8	- 7.7 ± 0.2	- 7.4 ± 0.2
W ₁	- 8.2	- 9.1	-	- 8.7 ± 0.3
L ₂ '	- 9.9	-11.0	-10.6 ± 0.3	-10.5 ± 0.4
Γ ₁	-12.0	-13.3	-12.6 ± 0.3	-12.8 ± 0.4

Table IV.

GaAs	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L ₃	- 0.9	- 0.9	- 0.8 ± 0.2	- 1.4 ± 0.3
X ₅	- 2.2	- 2.5	-	- 2.5 ± 0.3
W ₂	- 2.6	- 3.5	-	- 4.0 ± 0.2
Σ ₁ ^{min}	- 3.2	- 3.9	- 4.1 ± 0.2	- 4.4 ± 0.2
W ₁	- 6.0	- 6.6	-	- 6.6 ± 0.2
X ₃	- 6.4	- 6.8	- 6.8 ± 0.2	- 7.1 ± 0.2
X ₁	- 9.7	-11.4	-10.8 ± 0.4	-10.7 ± 0.3
Γ ₁	-12.0	-13.8	-11.9 ± 0.6	-13.8 ± 0.4

Table V.

GaP	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L ₃	- 0.9	- 1.0	-	- 1.4 ± 0.3
X ₅	- 2.3	- 2.5	-	- 2.7 ± 0.2
W ₂	- 3.2	- 3.7	-	- 3.6 ± 0.2
Σ ₁ ^{min}	- 3.8	- 4.1	- 4.2 ± 0.3	- 4.0 ± 0.2
W ₁	- 5.4	- 6.6	-	- 6.5 ± 0.2
X ₃	- 5.8	- 6.9	- 7.0 ± 0.3	- 6.9 ± 0.2
X ₁	-11.5	-10.9	-	- 9.6 ± 0.3
Γ ₁	-13.0	-13.6	-12.0 ± 0.6	-13.2 ± 0.4

Table VI

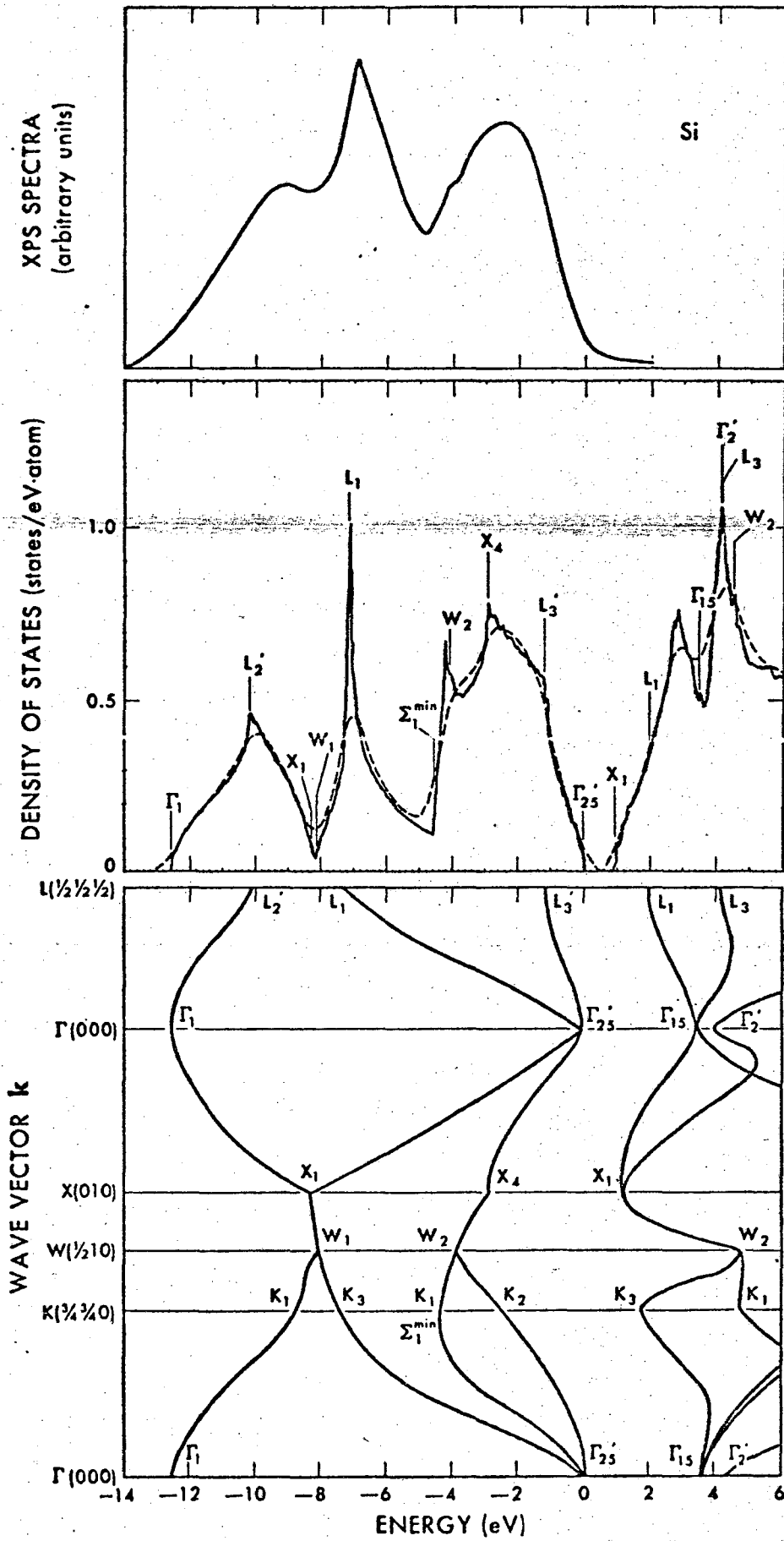
ZnSe	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L ₃	- 0.9	- 0.9	-	- 1.3 ± 0.3
X ₅	- 1.5	- 2.1	-	- 2.1 ± 0.3
W ₂	- 2.0	- 3.3	-	- 2.6 ± 0.2
Σ ₁ ^{min}	- 2.7	- 3.8	- 4.0 ± 0.3	- 3.4 ± 0.4
W ₁	- 3.4	- 5.3	-	- 5.2 ± 0.2
L ₁	- 3.8	- 5.9	- 5.7 ± 0.3	- 5.6 ± 0.3
X ₁	-13.2	-14.2	-	-12.5 ± 0.4
Γ ₁	-14.2	-15.8	-	-14.5 ± 0.6

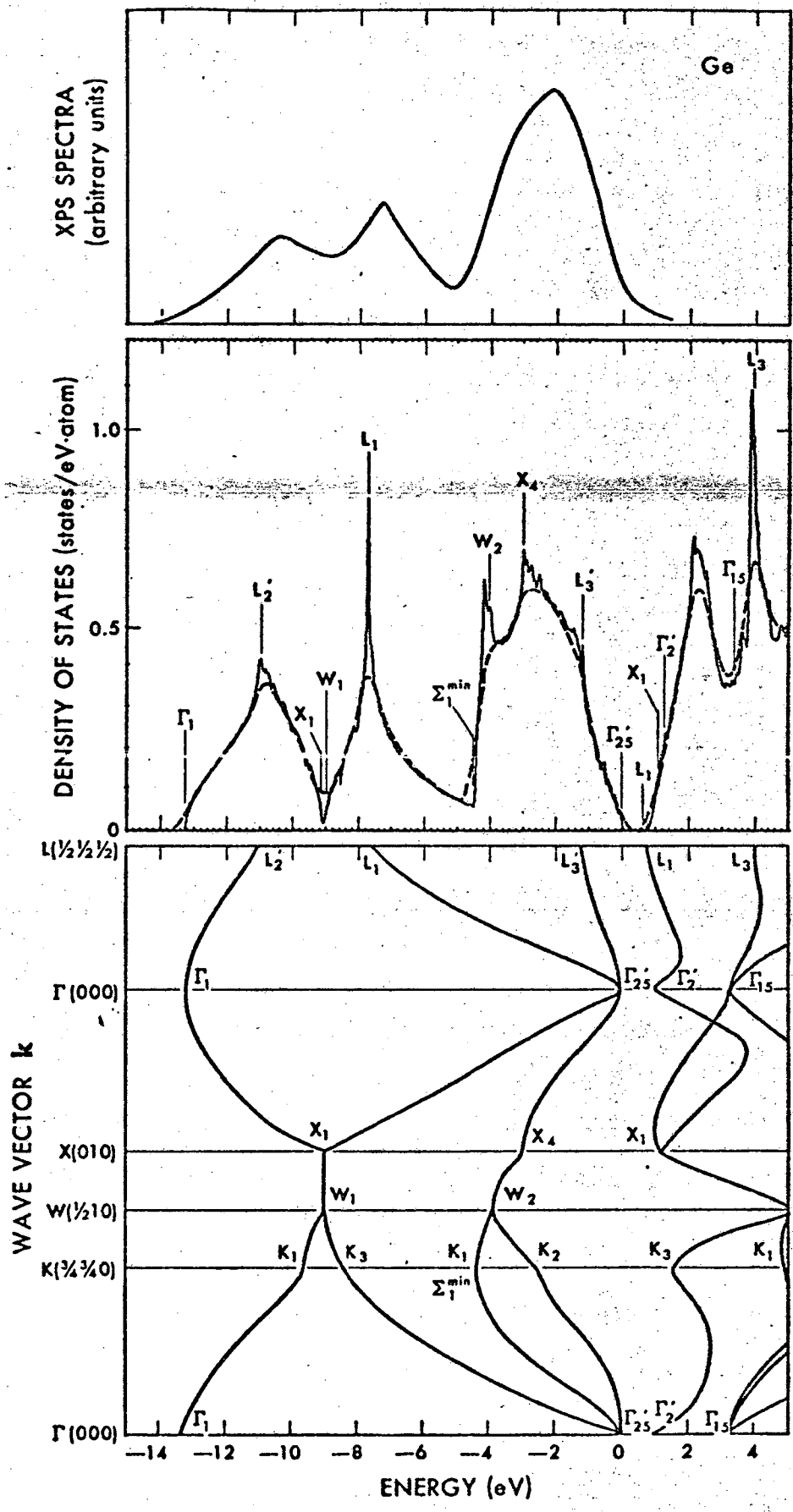
Table VII.

InSb	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L ₃	- 0.6	- 1.2	-	- 1.4 ± 0.2
X ₅	- 1.4	- 2.1	-	- 2.4 ± 0.4
W ₂	-	- 2.8	-	- 3.1 ± 0.2
Σ ₁ ^{min}	- 2.1	- 3.2	- 3.3 ± 0.3	- 3.4 ± 0.2
L ₁	- 4.9	- 5.7	-	- 5.9 ± 0.2
X ₃	- 5.4	- 6.2	- 6.2 ± 0.3	- 6.4 ± 0.2
X ₁	- 7.6	- 9.5	- 9.6 ± 0.3	- 9.5 ± 0.2
Γ ₁	- 8.9	-11.3	-10.9 ± 0.5	-11.7 ± 0.3

Table VIII.

CdTe	Theory		Experiment	
	Old ^a	New	UPS ^b	XPS ^c
L ₃	- 0.4	- 1.0	- 0.7 ± 0.3	- 0.9 ± 0.3
X ₅	- 1.0	- 1.5	-	- 1.8 ± 0.2
W ₂	- 1.4	- 2.0	-	- 2.2 ± 0.3
Σ ₁ ^{min}	- 2.0	- 2.7	- 2.9 ± 0.3	- 2.7 ± 0.3
W ₁	- 2.6	- 4.3	-	- 4.5 ± 0.1
X ₃	- 2.9	- 4.6	- 4.8 ± 0.2	- 5.2 ± 0.2
X ₁	-12.5	-10.6	- 8.8 ± 0.3	-
Γ ₁	-12.9	-11.8	-10.8 ± 0.6	-





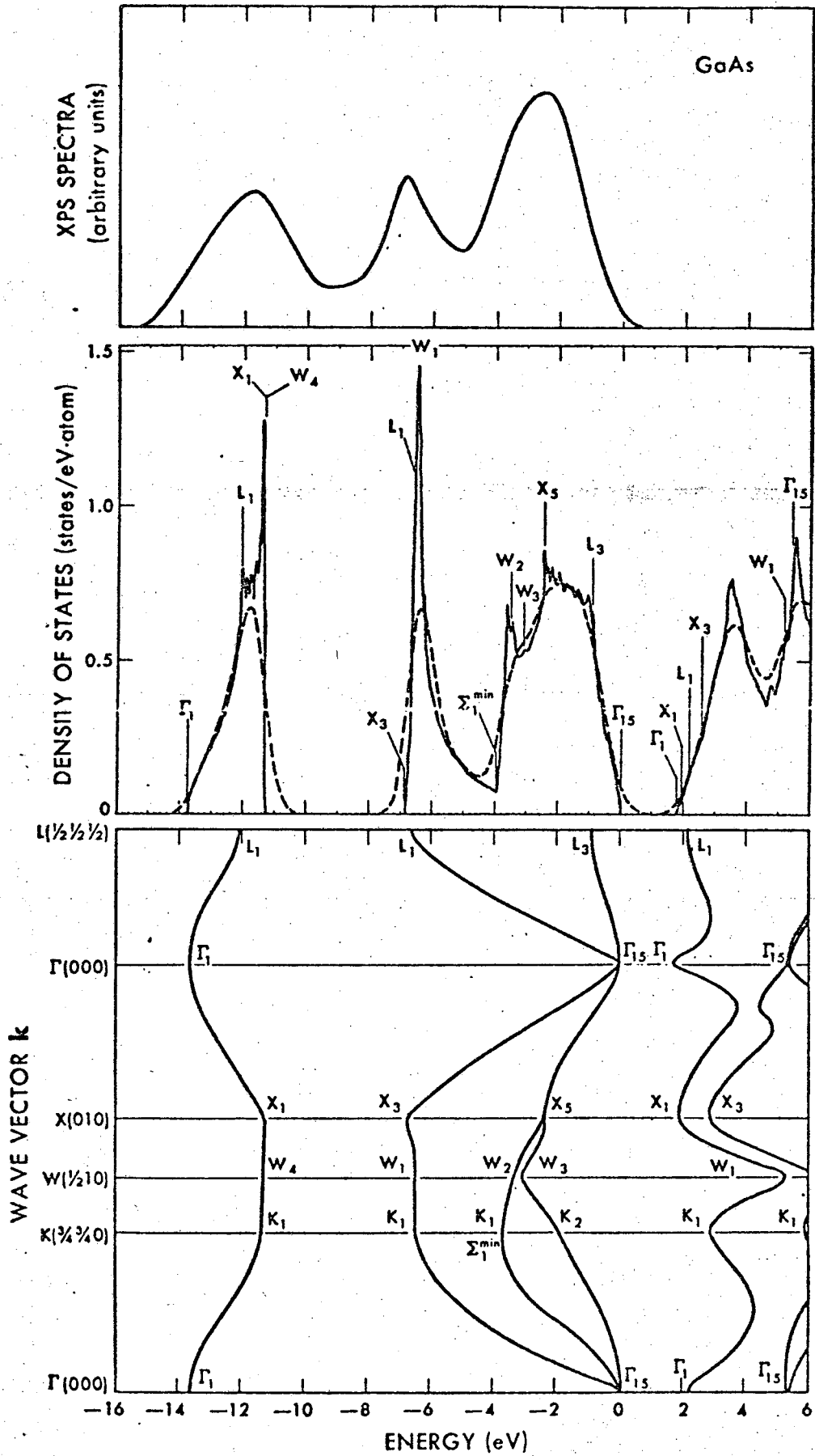
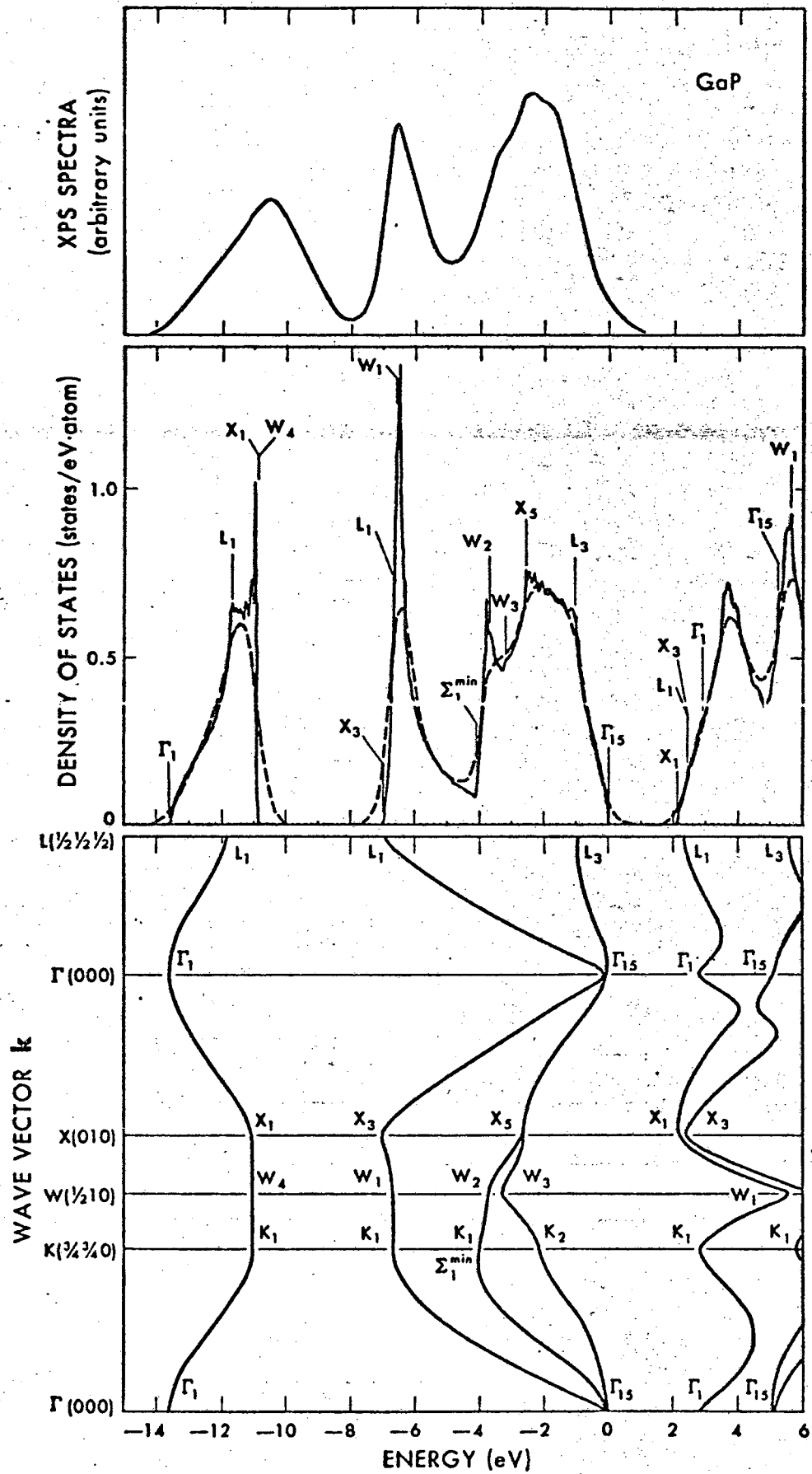


FIG. 4



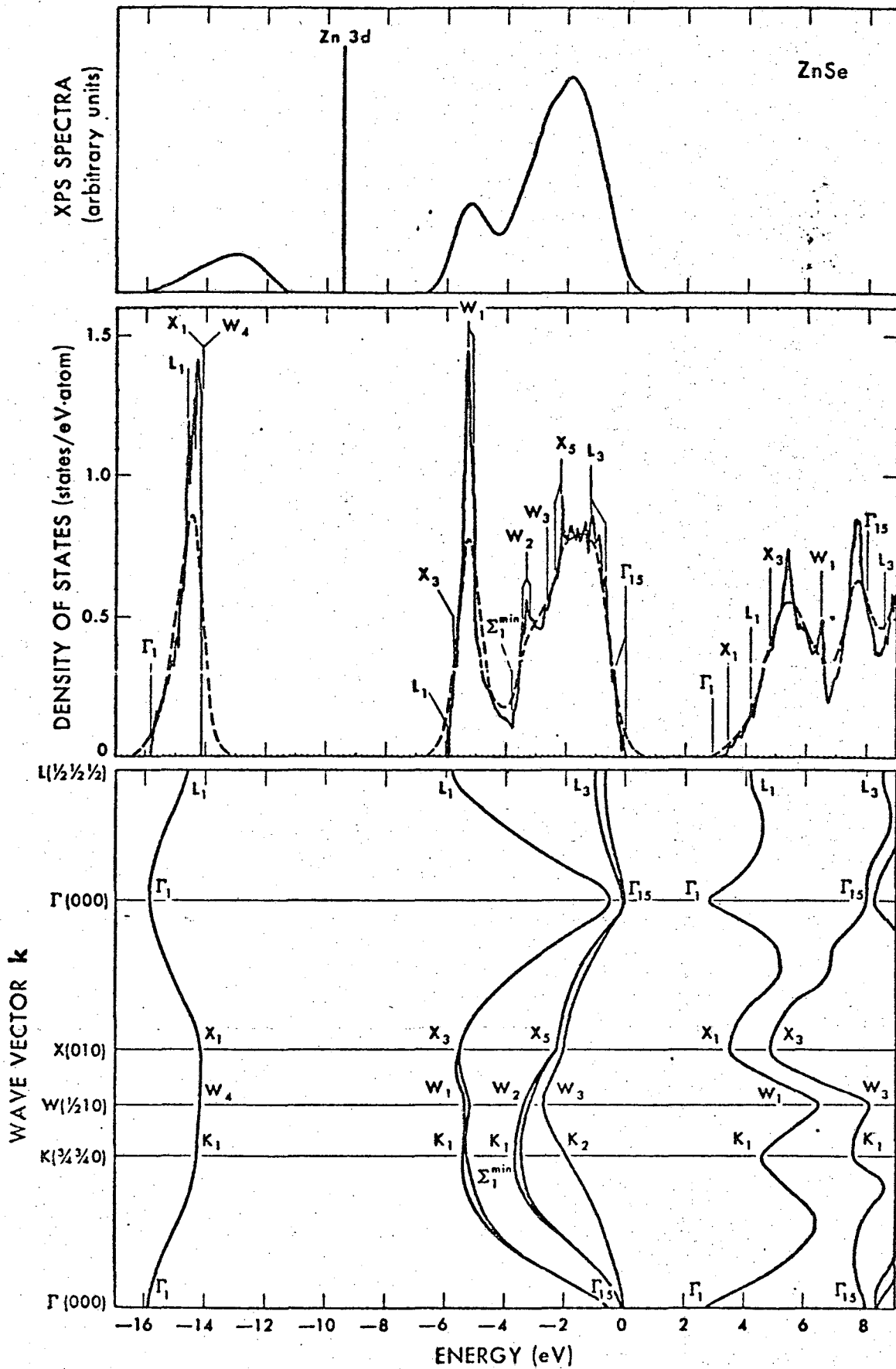


FIG. 6

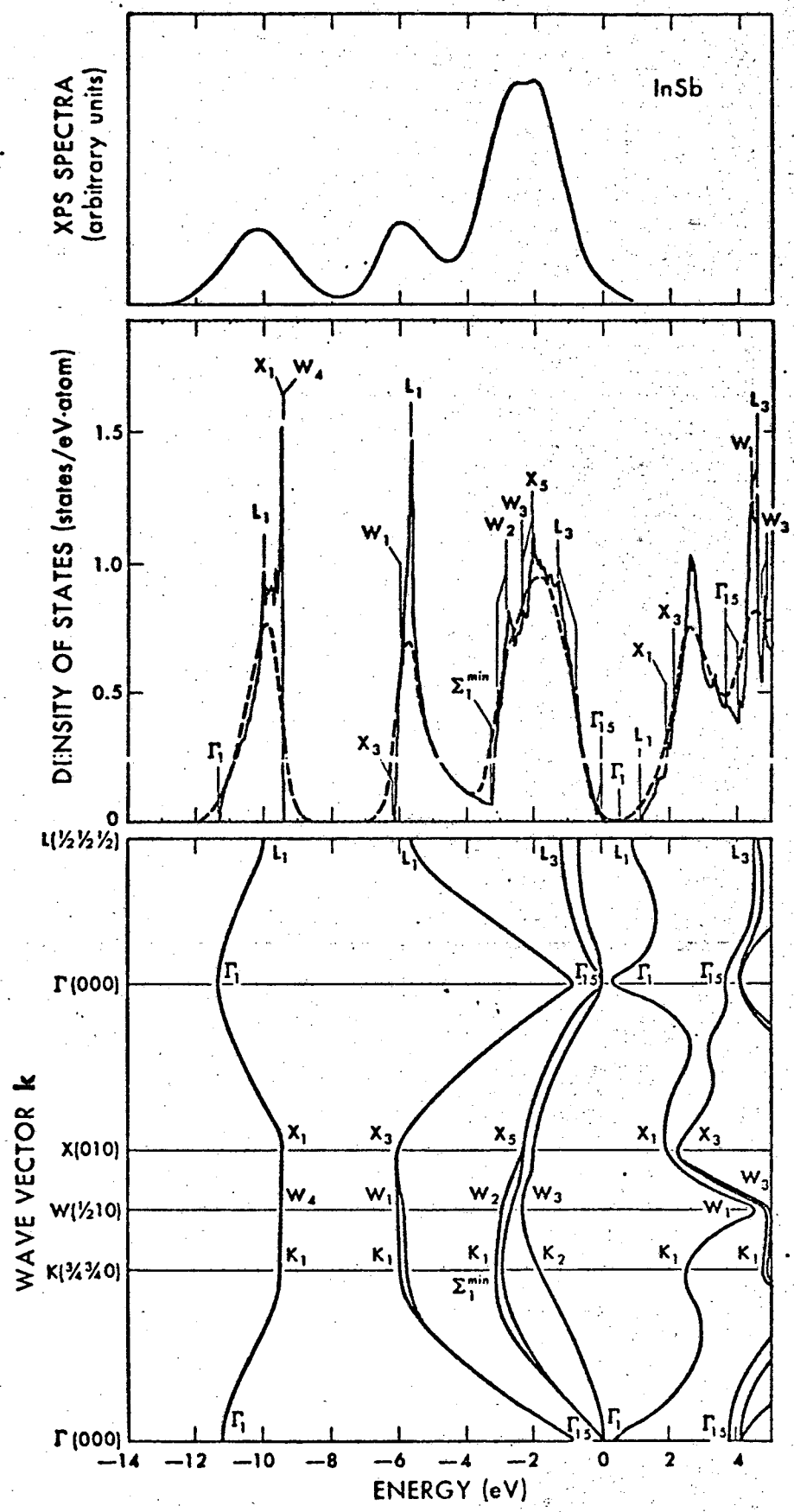
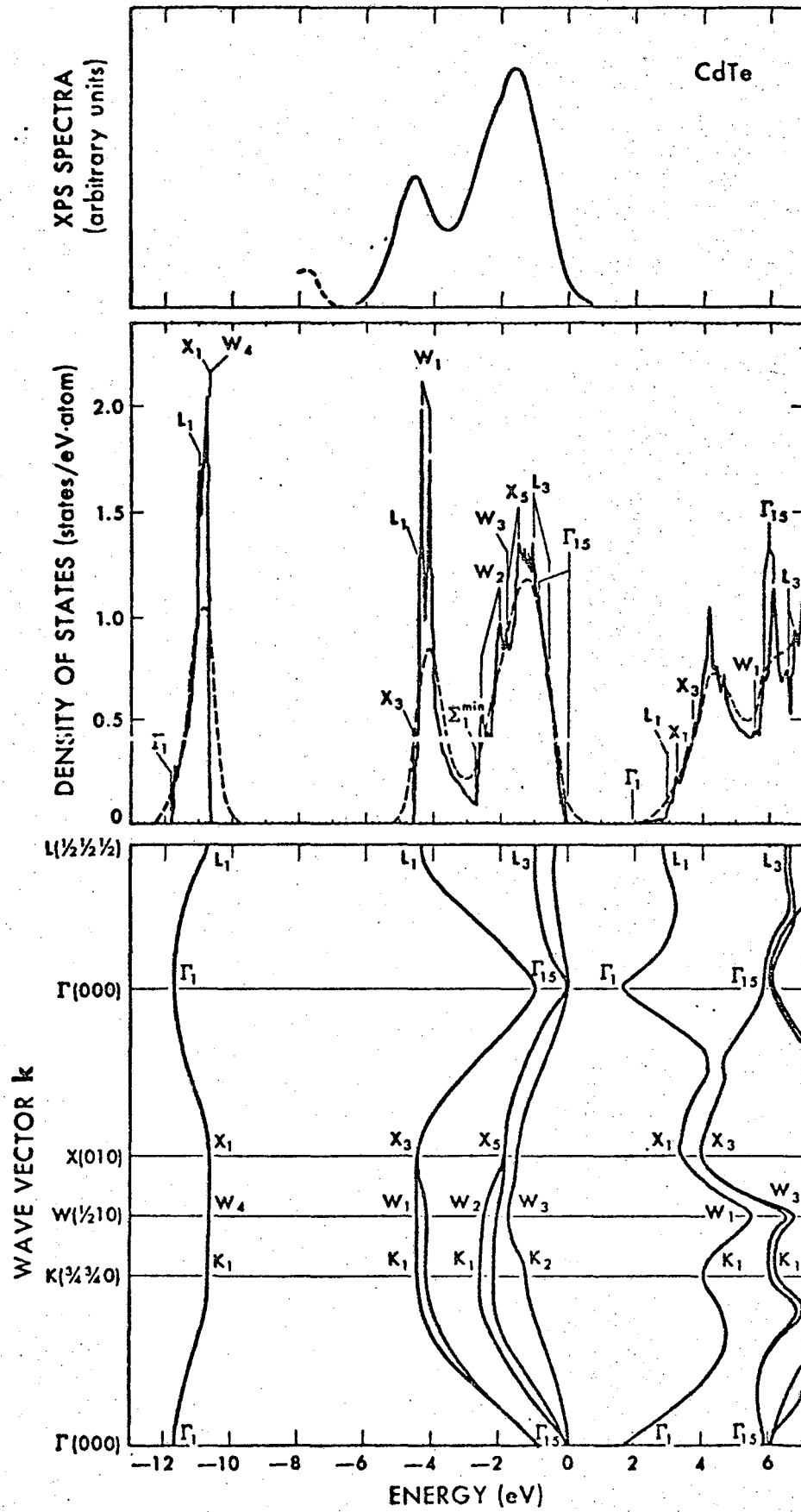


FIG. 7



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