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Photoemission Study of the Electronic Structure of CdTe*†

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ABSTRACT

We have performed photoemission experiments which provide an independent check of a number of band structure assignments of optical structure in CdTe. We find that a majority of the previous assignments are incorrect.

The study of the band structure of semiconductors has been revolutionized by the reflectance experiments dating from Philipp and Taft[1] in 1959 and their interpretation in terms of optical critical points by Phillips[2] in 1960. Due to the apparent initial success in interpreting the optical data and the realization that the principles of interpretation were correct, strong optimism developed as to the certainty with which key interband energy separations could be inferred from the optical data. The interpretation of the optical data for the column IV semiconductors was directly extrapolated to III-V, II-VI and even

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II-VI compounds.[3,4] These critical point assignments became the basis for subsequent empirical pseudopotential band calculations.[4,5,6] This procedure has formed a somewhat closed cycle which reinforces itself without, in many cases, bringing sufficient new experimental data to bear on the problem so that independent checks can be made on the optical assignments and band calculations. Since photoemission studies determine the absolute energies of the initial and final states in an optical transition,[5,7] they provide such an independent check.

In this paper, results from a detailed photoemission study of CdTe are reported. We view this as a good test case of the present interpretation of optical data, since CdTe (a II-VI compound with zinc blende crystal structure) lies rather well removed from the column IV semiconductors. We find that significant misinterpretations have been made in the past assignments of optical structure.[3,4,6] Because of this misinterpretation of optical data, empirical pseudopotential calculations[6] based on this data inevitably are in error in some respects.

The photoemission experiments were performed on single crystals cleaved in a high-vacuum chamber[8] at a pressure of 10^{-9} torr, and in a low-vacuum chamber[9] at a pressure of 10^{-4} torr. A total of 12 cleavages were obtained from four single crystals. Each cleavage had a surface area of about 1.0 cm^2 and a thickness of 2 to 4 mm. Cleaving in the lower vacuum resulted in an electron affinity more than a volt lower than for the high-vacuum-cleaved sample; however, no other significant changes in the structure were observed. Measurements were made for $5.4 \leq h\nu \leq 21.2$ eV; however, for the sake of brevity, only

those for $5.4 \leq h\nu \leq 9.2$ eV from the low-vacuum-cleaved samples will be discussed here. A complete report of all experiments will be published later.[10]

Representative energy distribution curves (EDC) are given in Figs. 1 and 2. The zero of energy is taken at the valence band maximum. Since the EDC have been normalized to yield, an absolute scale [electrons/photon/eV] is placed on the ordinate. Before discussing the rich structure in the EDC, it is important to eliminate the possibility that the structure is due to transport effects. Kane[11] has recently suggested that, due to the combined effects of (1) low group velocity at critical points and (2) phonon scattering, band structure may impress itself on photoemission through transport effects rather than through optical excitation probability. As Kane points out, this will result in structure which does not move as the photon energy is varied, but which is stationary in energy for $h\nu$ greater than some minimum value. As can be seen from Figs. 1 and 2, none of the structure observed in CdTe falls into this category. Rather, peaks appear and disappear rather abruptly. Thus we can rule out the possibility that the structure is due to transport effects.

Because of the abrupt manner in which the structure appears and disappears as $h\nu$ changes and because there is no structure which either is stationary or which moves by an amount equal to the change in $h\nu$, it is clear that the structure is due to direct transitions.[9,12] This conclusion has been well confirmed by detailed calculations.[9,10] Recognizing this character of the photoemission structure, our purpose here

will be to (1) relate the structure in the EDC to that in the optical data, (2) confirm or refute previous assignments of the optical structure, (3) establish the absolute energies of the initial and final states involved in the optical transitions, and (4) provide suggestions as to major features of the band structure.

There are four pieces of structure in the EDC (see Figs. 1 and 2): two peaks labeled P1 and P2 and two shoulders labeled S1 and S2. P1 rises swiftly with increasing hν until it reaches a maximum at a final state energy of 5.4 eV for hν = 6.8 eV. There is a corresponding peak in the reflectance spectra at hν = 6.8 eV. P1 becomes less distinct for hν near 7.6 eV, sharpens for $8.0 \leq h\nu \leq 8.4$ eV and disappears abruptly for hν > 8.4 eV. The abrupt disappearance of P1 indicates that the lower limit of the valence bands has been reached. A second peak P2 behaves in a somewhat similar manner, reaching a maximum for $7.6 \lesssim h\nu \lesssim 8$ eV. Since the values of photon energy at which the peaks reach their maxima are to be associated with peaks in the optical data[13] (see Table I), one can obtain the absolute values of the initial and final states involved in the optical transitions.

P1 and P2 are associated with the optical peaks at 6.8 and 7.6 eV (see Table I). Previously, this structure in the optical data has been assigned[3,4,13] to transitions from the spin-orbit split valence band L_3^v to the conduction band L_3^c. This assignment requires the final energies to be the same for both components of the transition. From Figs. 1 and 2 and the discussion above, it is clear that this is not the case. The final state for the 6.8 eV optical peak lies at 5.4 eV and

that for the 7.6 eV optical peak lies at about 6.2 eV. Thus the assignment of the two optical peaks to the L transitions can at once be discarded.[14]

Previous workers[3,4,6,13] are in agreement that the optical peak at $h\nu = 5.4$ eV is due to a transition near X; however, no strong structure was assigned to the $X_5^v \rightarrow X_3^c$ transition. We suggest instead that the peaks at 5.4 and 6.8 eV are due to the $X_5^v \rightarrow X_1^c$ and $X_5^v \rightarrow X_3^c$ transitions (it is impossible to determine from our experiment alone the ordering of the levels X_1^c and X_3^c). This point is extremely important for the pseudopotential band calculations since the $X_1^c - X_3^c$ splitting is taken as a measure of the antisymmetric potential used in those calculations. Cohen and Bergstresser (hereafter referred to as CB) took this splitting to be 0.8 eV whereas the present results indicate a splitting of approximately three times that amount.

Since spin-orbit splitting is not seen in P2 (comparable splittings have been observed in other photoemission studies[16]) the 7.6 eV optical peak cannot be associated principally with L_3^v transitions or any transition in the vicinity of the Λ direction. Based on CB's band calculation, it seems likely that it is to be associated with the $K_1^v \rightarrow K_1^c$ transition; however, it may be due to transitions at more general regions in the zone.

The fact that P1 becomes less distinct for $h\nu$ near 7.6 eV, sharpens for $8.0 \leq h\nu \leq 8.4$ eV, and disappears abruptly for $h\nu > 8.4$ eV indicates coupling between the second condution band at X (X_3^c) and the lowest valence band at X (X_1^v). This locates the bottom of the valence band at 3.0 eV in good agreement with CB.

Let us now examine the two shoulders S1 and S2 in Figs. 1 and 2. Since the shoulders appear near the maximum energy they can only be due to transitions from states near the valence band maximum,[17] Γ_{15}^{v}. In this paper, Γ_{15}^{v} refers to the uppermost of the spin-orbit-split levels Γ_{15}^{v}. Thus we assign S1 to $\Gamma_{15}^{v} \rightarrow \Gamma_{15}^{c}$ transitions. Since S1 appears for $h\nu > 5.8$ eV, this locates Γ_{15}^{c} at 5.8 eV. A slight shoulder appears at 5.8 eV in the reflectance data of Cardona and Greenaway (see Table I). S2 appears abruptly for $h\nu > 8.7$ eV, placing the third Γ conduction band (either Γ_1 or Γ_{12}) at 8.7 eV. The edge of the broad optical structure labelled d_1 by Cardona and Greenaway[13] appears at about 8.7 eV.

A comparison of our assignments with those of Cardona and Greenaway can be obtained from Table I. It should be noted that in only one case (the 5.4 eV transition at X) are their assignments in agreement with the present work.

For the sake of summary and comparison, the transitions which we observe in the photoemission data are sketched onto the band structure of CB in Fig. 3. Since CB did not include spin-orbit splitting in their calculation, the effects of this splitting of the valence band were taken out of our data before it was placed on Fig. 3. Good agreement is found near X in the valence band and, perhaps, near K. However, we find Γ_{15}^{c} 0.5 eV lower than CB calculated, and we find the $X_1^c - X_3^c$ splitting to be three times larger than their result. However, since the antisymmetric potential was set by the $X_1^c - X_3^c$ splitting, and since this splitting had been previously misinterpreted, this difference is due to misassignment of the optical data.

This study shows that the assignment of optical structure on the basis of extrapolation from the column IV elements is very unreliable. In the present study, 4 out of 5 previous assignments for CdTe are found to be in error. The pseudopotential band calculation[6] has proved to be quite helpful for a qualitative interpretation of our experimental data; however, our work has uncovered quantitative inaccuracies in certain features of this calculation. It is clear that some of the inadequacies of the pseudopotential band structure would flow improperly interpreted experimental data.

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TABLE I - Correlation of Optical and Photoemission structure for $5 < h\nu < 9.5$ eV

$h\nu$ at which structure appears	Label of photoemission structure in Figs. 1 and 2	Energy of final state	Energy of initial state	Assignment suggested by this work	Previous assignment Refs. 3, 4, 6, 13
		A. Major Structure (PEAKS)			
5.4	(lies too low in energy for electrons to escape into vacuum)	(4.0 eV)	(-1.4)	first X transition[a] ($X_5^v \rightarrow X_1^c$)	$X_5^v \rightarrow X_1^c$
6.8	P1	5.4	-1.4	second X transition ($X_5^v \rightarrow X_3^c$)	$L_3^v \rightarrow L_3^c$
8.0	P2	6.2	-1.8	K_1^v to K_1^c and/or transitions at more general points in the zone	$L_3^v \rightarrow L_3^c$
		B. Minor Structure (SHOULDERS)			
5.2	--	--	--	--	$\Gamma_{15}^v \rightarrow \Gamma_{15}^c$
5.8	S1	5.8	0	$\Gamma_{15}^v \rightarrow \Gamma_{15}^c$	$X_5^v \rightarrow X_3^c$
8.7	S2	8.7	0	$\Gamma_{15}^v \rightarrow \Gamma_1^c$ or $\Gamma_{15} \rightarrow \Gamma_{12}^c$	threshold of d-band transitions

a. Since the photoemission experiment cannot determine the ordering of the levels X_1^c and X_3^c, the final state for the first X transition may be either X_1^c or X_3^c.

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14. It should be noted that the systematics of the optical data also argue against the previous assignment. Theoretically, it is expected (Ref. 15) that the spin-orbit splitting should be approximately the same for the series ZnTe, CdTe, and HgTe. Experimental confirmation (Ref. 13) is found for this in the splittings of the E_1 peaks: 0.56 eV (ZnTe), 0.56 eV (CdTe), and 0.62 eV (HgTe). However, for the transitions

References (cont'd)

assigned to $L_3^v \rightarrow L_3^c$ (E_1' peaks), the splittings are quite different: 0.53 eV (ZnTe), 0.38 eV (CdTe), and 1.25 eV (HgTe). The shapes and relative strengths of the E_1' peaks also vary considerably among the compounds, whereas this is not the case for the E_1 peaks.

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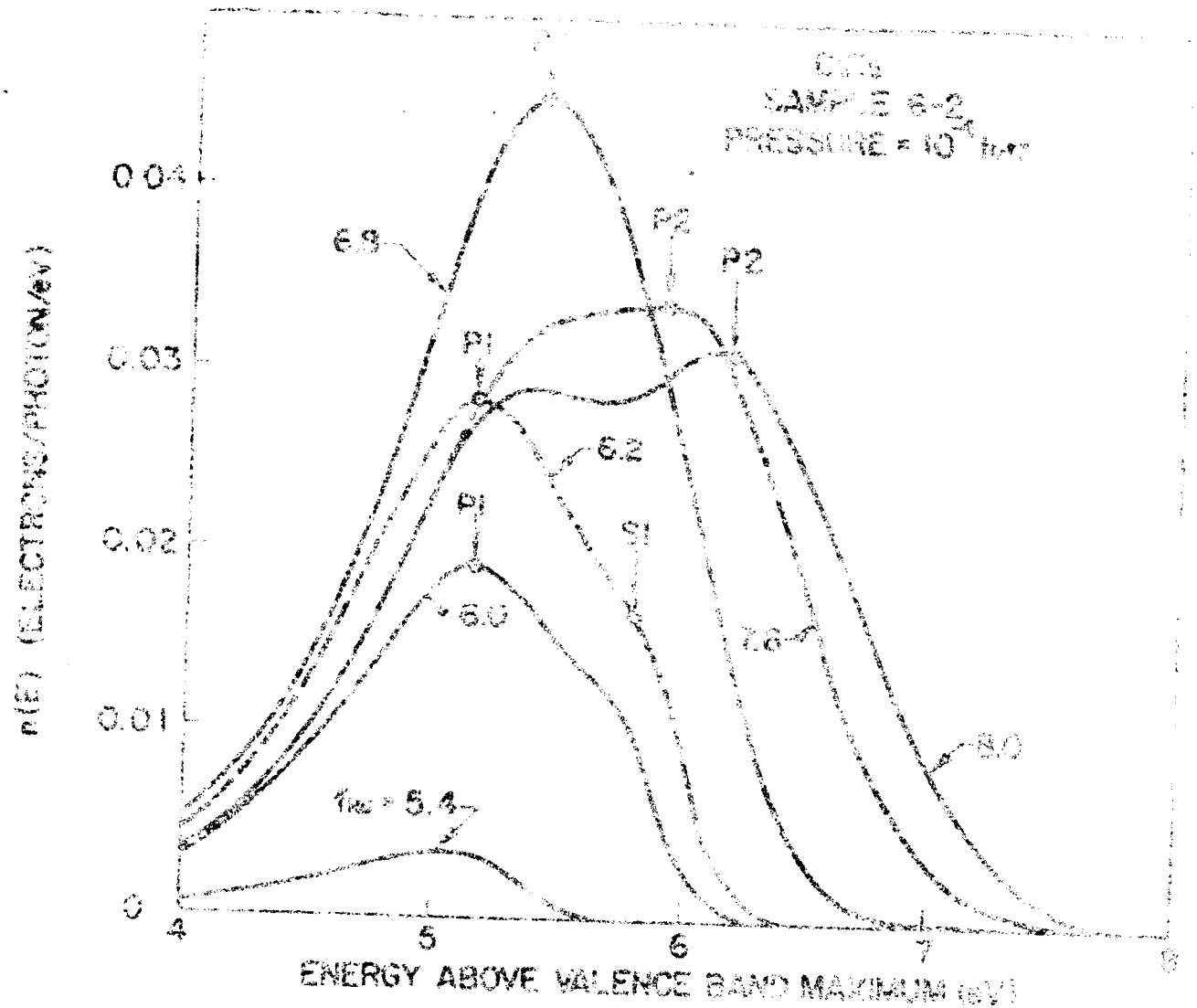
17. The fact that shoulders and not peaks are obtained in the EDC is also in agreement with this assignment since a M_0 critical point (Ref. 4) is to be expected.

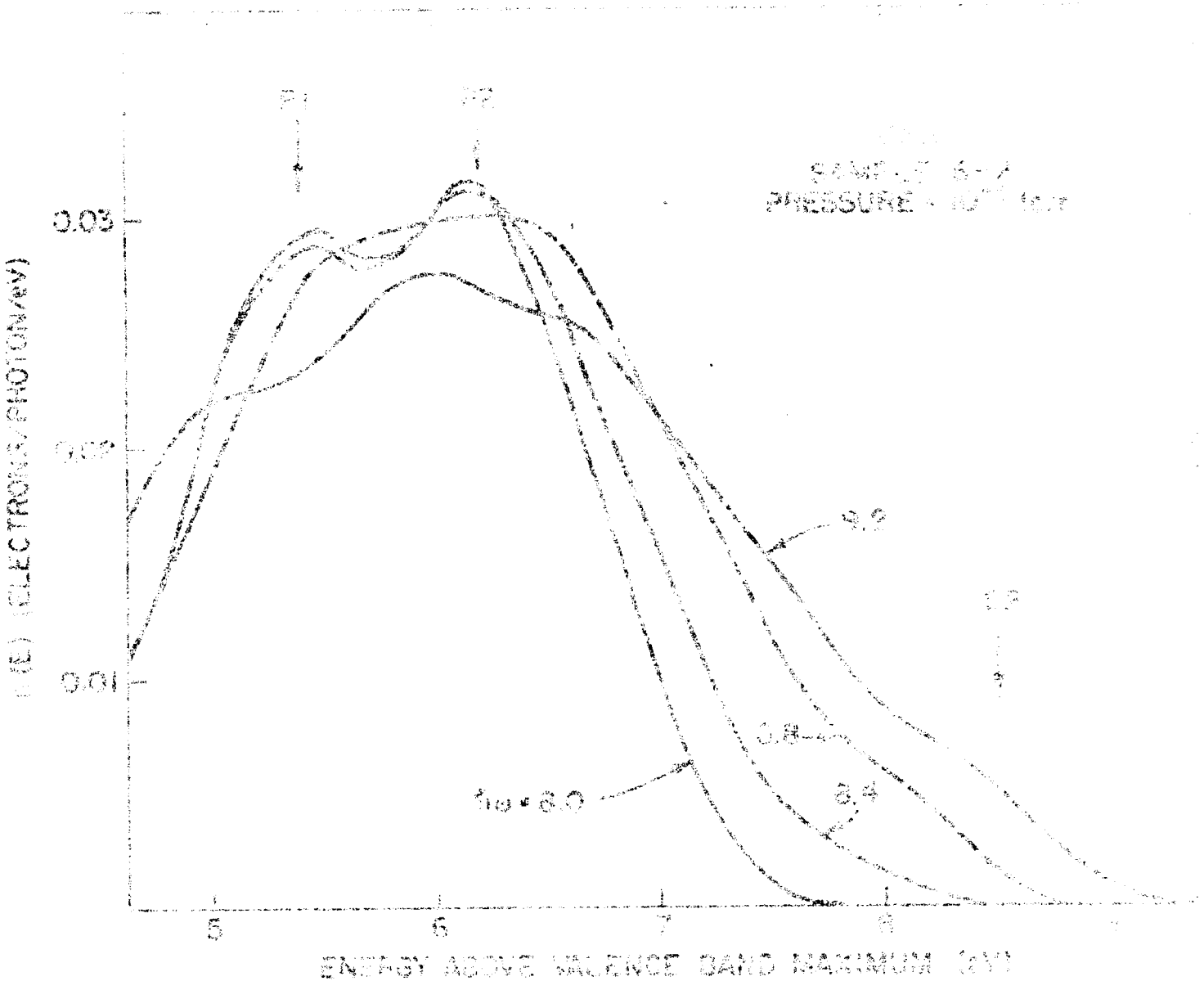
Figure Captions

1. Normalized energy distributions of the photoemitted electrons for the low-vacuum-cleaved sample of CdTe for $5.4 \leq h\nu \leq 8.0$ eV. The peaks P1 and P2 and shoulders S1 and S2 are discussed in the text.

2. Normalized energy distributions of the photoemitted electrons for the low-vacuum-cleaved sample of CdTe for $8.0 \leq h\nu \leq 9.2$ eV. The shoulder S2 and peaks P1 and P2 are discussed in the text.

3. Comparison of photoemission results for CdTe and the pseudopotential band structure calculated by Cohen and Bergstresser.[6] The solid lines are the calculated bands (the centers of gravity of spin-orbit-split levels); the cross-hatched areas joined by arrows indicate the transitions observed experimentally. The photon energy of the transition is indicated on the arrows. The states for the 8.0 eV transition (7.6 eV reflectivity peak) are dashed-in since it may involve states in more general regions of the zone. For this figure alone, the effects of spin-orbit splitting of the valence band have been subtracted out of the experimental results.


0.04
0.03
0.02
0.01
0
n(E) (ELECTRONS/PHOTON/eV)
6.9
P2
P2
P1
6.2
P1
S1
6.0
7.6
8.0
5.4
4
5
6
7
8
ENERGY ABOVE VALENCE BAND MAXIMUM (eV)


P1
P2
0.03
0.02
0.01
3.2
3.0
2.8
2.6
hν = 6.0
5
6
7
8
ENERGY ABOVE VALENCE BAND MAXIMUM (eV)