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[4] The errors involved are at most ~10%; see D. C. Wallace, Phys. Rev. 139, A877 (1965).

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[6] J. L. Feldman and G. K. Horton, to be published. The A in the anharmonic frequency shift also appears in the anharmonic specific heat at high temperature as $C_V = 3Nk(1-AT)$.

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$$\varphi(r) = \frac{6n\epsilon}{n-6}\left[\frac{1}{n}e^{-n(r/\sigma-1)} - \frac{1}{6}\left(\frac{\sigma}{r}\right)^6\right];$$

for $n = 14$ (1N), the dispersion curves lie about 2% below the Lennard-Jones $m = 13$ (1N) case. $n = 15$ (1N) gives a reasonable fit.

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PHOTOEMISSION STUDY OF THE ELECTRONIC STRUCTURE OF CdTe[†,‡]

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Cardona and Greenaway's identifications of the E_0', E_1', and $E_1'+\Delta_1$ peaks in the optical reflectivity spectrum of CdTe are contradicted by deductions drawn from photoemission measurements. New identifications of these peaks are proposed on the basis of these photoemission measurements and the results of empirically adjusted orthogonalized-plane-wave energy band calculations. Our theoretical band model for CdTe differs in some important respects from that derived by Cohen and Bergstresser using the empirical pseudopotential method.

The study of the band structure of semiconductors has been revolutionized by optical reflectivity measurements,[1] by the interpretation of optical spectra in terms of critical-point transitions,[2] by empirical energy-band calculations,[3-5] by electroreflectivity measurements,[6,7] and by piezoreflectivity measurements.[8] In view of the apparent success of the initial interpretations[2,3] of the optical spectra of Si and Ge, similar interpretations[9,10] have been made for a number of related materials, including III-V, II-VI, and even I-VII compounds. These interpretations form the basis of empirical (pseudopotential[3,4] and full-zone $\vec{k}\cdot\vec{p}$[5]) band calculations which are designed to support the interpretations upon which they are based. Interpretation of optical spectra and empirical band calculations form a closed cycle which can very easily perpetuate errors of interpretation and propagate such errors from one class of crystals to another. In order to discover and eliminate interpretational errors, it is essential to bring independent theoretical and experimental methods into play.

One of us (FH) has recently carried out an independent theoretical study[11] of the band structure of Si, Ge, and α-Sn which casts doubt on currently accepted interpretations[2-5,10] of the

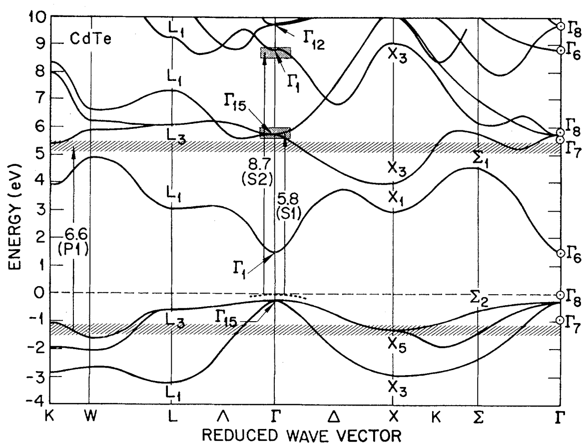

FIG. 1. Adjusted OPW energy band model for CdTe, with spin-orbit splitting neglected (except along right border and near valence band maximum). In the text, valence and conduction band levels are often distinguished by v and c subscripts which do not appear in above drawing. Note that the zero of energy is placed at Γ_8 rather than at Γ_{15}.

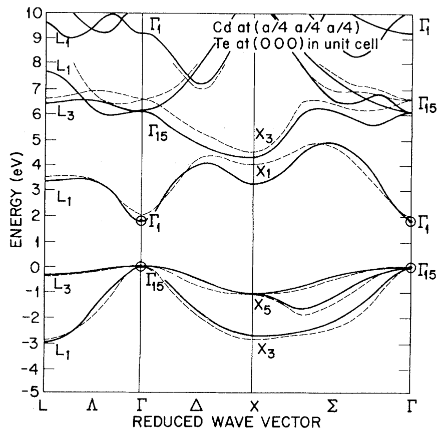

FIG. 2. Comparison of adjusted OPW energy-band model for CdTe (solid lines) with Cohen and Bergstresser's pseudopotential band model (dashed lines). Note that zero energy is now at Γ_{15}.

3.4-eV reflectivity peak in Si, and of spectral structure assigned to $\Gamma_{25'} \rightarrow \Gamma_{15}$ transitions (E_0'). The results of a similar study[12] of CdTe are depicted in Figs. 1 and 2. A fuller account of our theoretical work will be published elsewhere.[13]

Photoemission studies[14] provide an independent check on optical assignments and energy-band calculations since such studies determine the absolute energies of the initial and final states associated with a given set of interband transitions. In this Letter we will demonstrate the power of the photoemission approach by considering the two strong reflectivity peaks in CdTe near 6.8 and 7.6 eV which Cardona and Greenaway[15] (hereafter CG) denote by E_1' and $E_1' + \Delta_1$, and the partially resolved peak near 5.2 eV which they denote by E_0'. CG assign the 6.8- and 7.6-eV peaks to spin-orbit split $L_{3v} \rightarrow L_{3c}$ transitions, and the 5.2-eV peak to $\Gamma_{15v} \rightarrow \Gamma_{15c}$ transitions. As indicated in Table I, our photoemission results decisively contradict these assignments. Our independent theoretical and experimental studies cast doubt not only on CG's interpretation of key spectral features in CdTe, but also on their interpretation of analogous features in ZnTe, HgTe, and related crystals.[9,10,15] Our theoretical band model[12,13] for CdTe agrees quite well with Cohen and Bergstresser's pseudopotential band model[4] (cf. Fig. 2) so far as the valence bands and some conduction bands are concerned, but for other conduction bands there are differences comparable to those found in our earlier study of α-Sn.[11] It will require further experimental work to resolve these differences.

The photoemission experiments were performed on single crystals cleaved in a high-vacuum chamber[16] at a pressure of 10^{-9} Torr, and in a low-vacuum chamber[17] 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 1 eV lower than for the high-vacuum-cleaved sample[17,18]; however, no other significant changes in the structure were observed. Measurements were made for $5.4 \leq h\nu \leq 21.2$ eV. 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.[18] The experimental accuracy is ±0.2 eV.

Representative energy distribution curves (EDC) are shown in Figs. 3 and 4. The zero of energy is taken at the actual valence-band maximum (double group notation Γ_8). Since the spin-orbit splitting at the top of the valence band is 0.92 eV,[19] the zero of energy lies 0.3 eV above Γ_{15v}, as indicated in Fig. 1. Since the EDC have been normalized to yield, an absolute scale (electron/photon eV) is placed on the ordinate in Figs. 3 and 4.

Before discussing the rich structure in the

Table I. Correlation of photoemission and optical structure.

hν at which structure appears	Label of photoemission structure in Figs. 3 and 4	Energy[a] of final state	Energy[a] of initial state	Assignment suggested by this work	Previous assignment[c]
		A. Major Structure (peaks)			
6.6	P1	5.3	-1.3	zone edge W-K	$L_{3v} \to L_{3c}$
~7.2	P2[b]	6.2	-1.0	direct interband transitions	$L_{3v} \to L_{3c}$
8.0	P2[b]	6.2	-1.8	high densities of states in valence band and conduction band	$L_{3v} \to L_{3c}$
		B. Minor Structure (shoulders)			
5.2	---	---	---	----	$\Gamma_{15v} \to \Gamma_{15c}$
5.8	S1	5.8	0	$\Gamma_{15v} \to \Gamma_{15c}$	$X_{5v} \to X_{3c}$
8.7	S2	8.7	0	$\Gamma_{15v} \to \Gamma_{1c}^{\text{upper}}$	threshold of d-band transitions

[a] Energies are given in electron volts with respect to actual valence-band maximum (Γ_{8v}).

[b] The photoemission peak $P2$ is quite complex. A detailed analysis to be presented elsewhere [J. L. Shay and W. E. Spicer, to be published] suggests that $P2$ is due partly to direct transition (~7.2 eV), and partly to nondirect transitions which couple a high density of valence-band states near −1.8 eV with a high density of conduction-band states near 6.2 eV.

[c] For references, see text.

EDC, it is important to eliminate the possibility that the structure is due to transport effects. Kane[20] has recently suggested that, because of the combined effects of low group velocity at critical points and 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

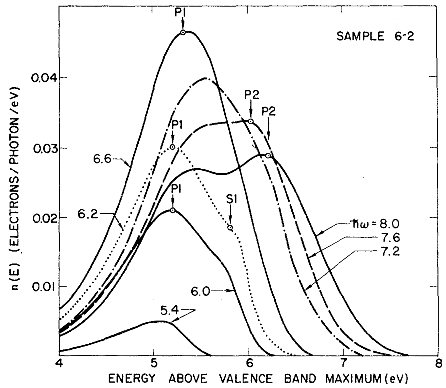

FIG. 3. Normalized energy distributions of the photoemitted electrons for the low-vacuum-cleaved sample of CdTe for $5.4 \leqslant h\nu \leqslant 8.0$ eV. The peaks $P1$ and $P2$ and the shoulders $S1$ and $S2$ are discussed in the text.

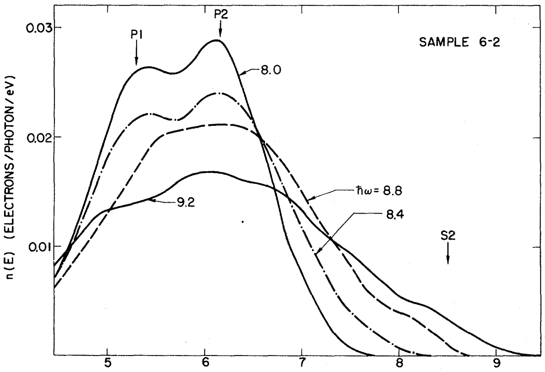

FIG. 4. Normalized energy distributions of the photoemitted electrons for the low-vacuum-cleaved sample of CdTe for $8.0 \leqslant h\nu \leqslant 9.2$ eV. The shoulder $S2$ and the peaks $P1$ and $P2$ are discussed in the text.

which is stationary in energy for $h\nu$ greater than some minimum value. As can be seen from Figs. 3 and 4, none of the structure observed in CdTe falls into this category. Rather, peaks appear and disappear quite abruptly. Thus, we can rule out the possibility that the observed structure is due to transport effects. Moreover, the abrupt manner in which $P1$ appears and disappears in the EDC indicates that this structure is due to direct transitions.[17,18,21]

Previous assignments[15] have assumed that the separation $\Delta_1 = 0.8$ eV between the 6.8-eV (E_1') and 7.6-eV ($E_1' + \Delta_1$) reflectivity peaks in CdTe is determined primarily by the spin-orbit splitting of the valence-band level L_{3v}, so that Δ_1 is in effect a measure of this splitting. If this were in fact the case, then the final state energies for the 6.8- and 7.6-eV reflectivity peaks would be the same, namely, that associated with L_{3c}. However, a study of Fig. 3 shows that the final-state energies of these two peaks are <u>not</u> the same. Peak $P1$ with a final energy of 5.3 eV dominates the EDC for the first optical peak ($h\nu \approx 6.8$ eV), while for $h\nu = 7.6$ eV the energy distribution is drastically different, with few electrons at 5.3 eV and most at considerably higher energies ($P2$).

Thus, our photoemission measurements rule out the possibility that the 6.8- and 7.6-eV reflectivity peaks are due to transitions to the to the same final state. Since it is usually assumed that the spin-orbit splitting of L_{3c} is considerably smaller than that of L_{3v}, our results also show that at least one of these reflectivity peaks is not due to transitions near L. With a view to finding an alternative interpretation of these two peaks, we turn to the band-structure picture in Fig. 1. Consider first $P1$, which is strongest in photoemission at $h\nu = 6.6$ eV. The initial- (-1.3 ± 0.2 eV) and final-state ($+5.3 \pm 0.2$ eV) energy ranges for $P1$, as determined from our photoemission measurements, are depicted in Fig. 1 by the shaded strips. Although the initial states for $P1$ coincide with the valence band level X_5, there are no final states at or close to X for this transition (cf. also Fig. 2). When the spin-orbit splitting of L_{3v} is taken into account, there are valence-band levels at L at -0.3 and -0.9 eV, but these are well outside the initial energy range of -1.3 ± 0.2 eV (cf. also Fig. 2). Thus, $P1$ and the associated reflectivity peak at 6.8 eV do not arise from transitions close to L. If one examines the highest valence band and the next to the lowest conduction band throughout the zone (using Fig. 1 as a guide), and if one allows for the spin-orbit splitting of these bands, the most likely origin of $P1$ and the 6.8-eV reflectivity peak is interband transitions near the zone edges (neighborhood of the line joining W and K). Further theoretical work on this question is now in progress.

Before considering the photoemission peak $P2$, let us examine the shoulders $S1$ and $S2$ in Figs. 3 and 4. The abrupt manner in which both $S1$ and $S2$ appear in the EDC is characteristic of direct transitions.[17,18,21] Since these shoulders appear near the maximum energy, they can be due only to transitions from states near the valence band maximum (Γ_{8v}). For this reason $S1$ is assigned to transitions from Γ_{8v} to Γ_{7c}, that is, from the highest spin-orbit-split Γ_{15v} level to the lowest spin-orbit-split Γ_{15c} level (cf. Fig. 1). Since the spin-orbit splitting of Γ_{15c} is characteristic of Cd $5p$ orbitals, while that of Γ_{15v} is characteristic of Te $5p$ orbitals, the Γ_{15c} splitting is considerably smaller than the Γ_{15v} splitting,[22] and we make no serious error if the Γ_{15c} splitting is neglected altogether. (A similar argument suggests that the L_{3c} splitting is small compared with the L_{3v} splitting.) Accordingly, we will treat Γ_{15c} and Γ_{7c} interchangeably. Since $S1$ appears for $h\nu > 5.8$ eV, we conclude that $E(\Gamma_{7c}) - E(\Gamma_{8v}) = 5.8$ eV. Allowing for the 0.92-eV spin-orbit splitting of Γ_{15v},[19] $E(\Gamma_{15c}) - E(\Gamma_{15v}) = 5.8 + \frac{1}{3} \times 0.92 = 6.1$ eV. This value forms one of the three experimental bases for the band structure picture in Fig. 1.[12]

CG's assignment of the 5.2-eV structure (E_0') to $\Gamma_{15v} \rightarrow \Gamma_{15c}$ transitions is inconsistent with our photoemission data, which indicate that such transitions occur only for $h\nu > 5.8$ eV. We suggest instead that the slight shoulder at 5.8 eV in the reflectivity data[15] is due to Γ_{15v} (really Γ_{8v}) $\rightarrow \Gamma_{15c}$ transitions.

Finally, we note that $S2$ appears abruptly for $h\nu > 8.7$ eV, placing the third major Γ conduction band ($\Gamma_{1c}^{\text{upper}}$ or Γ_{12c}) about 8.7 eV above Γ_{8v} or about 9.0 eV above Γ_{15v}. In Fig. 1, $\Gamma_{1c}^{\text{upper}}$ and Γ_{12c} lie 8.8 and 9.7 eV, respectively, above Γ_{8v}, so that $S2$ is most likely due to $\Gamma_{8v} \rightarrow \Gamma_{1c}^{\text{upper}}$ (and related) transitions. The edge of the broad optical structure labeled d_1 by CG appears at about 8.7 eV. This edge may also be related to the $\Gamma_{8v} \rightarrow \Gamma_{1c}^{\text{upper}}$ threshold.

We now turn to the photoemission peak $P2$

which appeared in the EDC (Fig. 3) at photon energies corresponding to the 7.6-eV reflectivity peak in CG's data.[15] In order to clarify the nature of this 7.6-eV peak, we have remeasured the reflectivity spectrum of CdTe, and we find our experimental spectrum[18] to differ considerably from CG's. In particular, we find a peak near 7.6 eV which is much broader than CG's 7.6-eV peak, suggesting that the structure here may be due to two different sets of transitions, rather than to just one set, as assumed by CG. We also find the photoemission peak $P2$ to be quite complex. The detailed analysis of $P2$ will appear in a subsequent publication.[18] This analysis suggests that $P2$ arises partly from direct transitions at general points away from Γ at about 7.5 eV, and partly from nondirect transitions at about 8.0 eV which couple a high density of valence-band states near -1.8 eV to a high density of conduction-band states near 6.2 eV.

It is of considerable interest to note that the energy of the main reflectivity peak in CdTe, 5.4 eV,[15] corresponds almost exactly to our value $E(X_{3c})-E(X_{5v})=5.3$ eV, this being 1 eV greater than our value $E(X_{1c})-E(X_{5v})=4.3$ eV. This raises the question whether the main 5.4-eV peak (E_2) is actually due to $X_{5v}\rightarrow X_{1c}$ transitions as suggested by CG[15] and accepted by Cohen and Bergstresser,[4] or whether this peak involves other sets of interband transitions, including $X_{5v}\rightarrow X_{3c}$. This and related questions are currently being investigated.

In summary, our photoemission studies suggest that earlier interpretations[15] of the optical reflectivity spectrum of CdTe should be modified in a number of important respects, and that some features of the pseudopotential band structure of CdTe,[4] particularly the location of X_{1c}, X_{3c}, and Γ_{15c}, should be reconsidered in the light of our independent theoretical and experimental findings (cf. Fig. 2).

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‡Based in part on a dissertation submitted by Joseph L. Shay to Stanford University in partial fulfillment of the requirements for the Ph.D. degree.

*National Science Foundation Predoctoral Fellow.

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[12] The energy-band picture for CdTe shown in Fig. 1 was obtained by methods similar to those described in Ref. 11. A first-principles OPW energy band structure was calculated by standard methods, and this structure was then modified slightly by a systematic empirical adjustment procedure so that the most reliably known experimental transition energies (in our opinion) were reproduced exactly. In practice, the empirical adjustment was quite small, corresponding roughly to a change by a few percent of the difference between the crystal potential and the orthogonality terms in the OPW secular equation. After carefully investigating a variety of alternative approaches, we concluded that a satisfactory and quite flexible adjustment procedure

could be based on only three parameters such as the Cd-ion core shift $\Delta E^{\mathrm{core}}(\mathrm{Cd})$, the Te-ion core shift $\Delta E^{\mathrm{core}}(\mathrm{Te})$, and the shift in the symmetric component of the [111] Fourier coefficient of crystal potential away from its first-principles value, $\Delta v_s(111)$. Here $\Delta E^{\mathrm{core}}(\mathrm{Cd/Te})$ denotes a common shift of all Cd/Te-ion core levels away from their respective first-principles values. The adjusted band structure shown in Fig. 1 was so constructed that the following three experimental transition energies were reproduced exactly: $E(\Gamma_{1c})-E(\Gamma_{15v}) = 1.8$ eV {direct band gap, based on electroreflectivity data [M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967)]}; $E(L_{1c}) -E(L_{3v}) = 3.6$ eV {based on optical [M. Cardona and D. L. Greenaway, Phys. Rev. 131, 98 (1963)] and electroreflectivity [Cardona, Shaklee, and Pollak, loc. cit.] data}; and $E(\Gamma_{15c})-E(\Gamma_{15v}) = 6.1$ eV (based on present interpretation of $S1$ shoulder in our photoemission data). Further theoretical work now in progress is aimed at including the spin-orbit splitting throughout the zone and at determining the complex dielectric response function for CdTe.

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NEW APPROACH TO LATTICE DYNAMICS APPLIED TO SOLID He^3 AT 0°K

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The expansion of a crystal potential in terms of a set of three-dimensional polynomials orthogonalized with respect to the weight function $f^2(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) \exp[(\vec{r}_i-\vec{R}_i)\cdot G_{ij} \cdot(\vec{r}_j-\vec{R}_j)]$ is shown to be a logical generalization of the previously introduced self-consistent harmonic approximation which is particularly appropriate for highly anharmonic systems. Explicit expressions for the calculation of the ground-state energy and phonon spectrum of a crystal at 0°K are given and certain numerical results for solid He^3 at 0°K are presented.

The theory of the self-consistent harmonic approximation was introduced in a previous Letter.[1] This theory combined the idea, originally due to Born,[2] of finding the optimum harmonic Hamiltonian

$$H^{(h)} = -\tfrac{1}{2}\lambda^2 \sum (\nabla_i^{\alpha})^2 + V_0 + \tfrac{1}{2}\sum q_i^{\alpha} \Phi_{ij}^{\alpha\beta} q_j^{\beta}/\lambda^2 \tag{1}$$

with which one can approximate a true crystal Hamiltonian

$$H = -\tfrac{1}{2}\lambda^2 \sum (\nabla_i^{\alpha})^2 + \tfrac{1}{2}\sum_{i\neq j} V_{ij} \tag{2}$$

with certain computational techniques introduced by the author.[3] The essential result is the self-consistent condition that one should choose $\Phi_{ij}^{\alpha\beta} = \lambda^2 \langle 0|\nabla_i^{\alpha}\nabla_j^{\beta} V|0\rangle/\langle 0|0\rangle$ in order to minimize $E_0 = \langle 0|H|0\rangle/\langle 0|0\rangle$.

In the above, λ^2 is an expression for the mass, q_i^{α} is the αth Cartesian component of the displacement of the ith particle, whose coordinate is $\vec{r}_i$, from its equilibrium position $\vec{R}_i$, $V_{ij} = V(|\vec{r}_i - \vec{r}_j|)$ is a suitable interatomic potential, and $V = \frac{1}{2}\sum_{i\neq j} V_{ij}$. The ground-state eigenfunction of $H^{(h)}$ is given by $|0\rangle \propto \exp[-\frac{1}{2} q_i^{\alpha} G_{ij}^{\alpha\beta} q_j^{\beta}/\lambda^2]$, where $\mathbf{G}^2 = \Phi$.

While one could probably calculate the ground-state properties of a substance with the anharmonicity of, for example, solid neon using perturbation theory based upon the eigenfunctions of $H^{(h)}$, it is clear that the Gaussian character of $|0\rangle$ will not at all be adequate for a treatment of highly anharmonic systems such as solid helium. A generalization of theory which remedies this deficiency will be presented in the following.

If one considers the identity

$$\int f(x) H_n(x) e^{-x^2} dx = \int \left[\frac{d^n}{dx^n} f(x)\right] e^{-x^2} dx,$$

where H_n is a Hermite polynomial, it is clear that a term of the form $\langle 0|\nabla_i^{\alpha}\nabla_j^{\beta} V|0\rangle$ is proportional to the second term in the expansion