over 0.12 eV on either side of the edge E_G, the integration had to be carried out over an interval A-B, only slightly larger than the range of Δn. A and B are determined from the requirement that the total contribution from regions outside A-B should not exceed 1% of the integral over A-B

$$\int_0^A \frac{\Delta\alpha(\omega')d\omega'}{\omega'^2-\omega^2} + \int_B^\infty \frac{\Delta\alpha(\omega')d\omega'}{\omega'^2-\omega^2}$$
$$\leq 0.01 \int_A^B \frac{\Delta\alpha(\omega')d\omega'}{\omega'^2-\omega^2}, \quad (A2)$$

even for $\hbar\omega = E_G \pm 0.12$ eV. Calculations show that $A = E_G - 0.125$ eV, and $B = E_G + 0.30$ eV, satisfy the inequality of Eq. (A2).

Aside from this question of convergence, an estimate must be made for the contributions from interband transitions above the fundamental edge. The next

reflectance response comparable in strength to the response at 0.8 eV was observed in germanium at 2.11 eV. Approximating this response by assuming a constant $\Delta\alpha = 5 \times 10^2$ cm^{-1} between the photon energies $E_1 = 2.05$ eV and $E_2 = 2.15$ eV, an upper limit for the contribution δn of this transition to the refractive index at the high-energy end $E_0 = E_G + 0.12$ eV is obtained by

$$\delta n(E_0) = \Delta\alpha \frac{hc}{\pi} \int_{E_1}^{E_2} \frac{dE'}{E'^2 - E_0^2} < \Delta\alpha \frac{hc}{\pi}$$
$$\times \frac{(E_2 - E_1)}{E_1^2 - E_0^2} = 9.4 \times 10^{-5}. \quad (A3)$$

This proves that even the closest transition of considerable response contributes only amounts of the order of 1% to the Δn in the region of the fundamental edge.

Photoemission Investigation of the Band Structure of PbTe[†]

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Measurements of the spectral distribution of photoemissive quantum yield and the energy distribution of photoemitted electrons from PbTe for 5.0 eV $< h\nu < 11.5$ eV are reported. The electron affinity is found to be 4.6±0.3 eV. Regions with high density of states are located 0.7 and 1.2 eV below the valence-band maximum and assigned to the (L_4^+, L_5^+) and L_6^+ symmetry points, respectively. By using the photoemission data and Cardona and Greenaway's optical data, the L_6^- and (L_5^-, L_4') conduction-band points are located approximately 1.3 eV above the valence-band maximum. A high-density point is found 2.4 eV below the valence-band maximum. Evidence is presented that this high-density point is not due solely to structure near the L point.

I. INTRODUCTION

IN recent years there has been considerable interest in the band structure of PbTe and the other lead salts. First-principle theoretical calculations have proved difficult because of problems in determining both the core and valence potentials. However, the recent work of Pratt and Ferreira and of Conklin, Johnson, and Pratt, which uses only a minimum of experimental data, has produced reasonable results at the L point.[1]

By making use of the Shubnikov–de Haas method, and other experimental data, the band structure has been determined in detail at the band extrema which are

located at the L point.[2,3] Through consideration of the interactions with other bands at the L point necessary to give the observed band structure, Cuff *et al.*[4] have estimated the location of the other bands near the L-point extrema. Kleinman and Lin[5] have used the data at the extrema as well as the optical data of Cardona and Greenaway[6] as the basis for a pseudopotential band calculation.

The only experimental studies previously available which gave direct information concerning the band structure away from the extrema are contained in the optical studies of Cardona and Greenaway.[6] These

[1] G. W. Pratt, Jr., and L. G. Ferreira, *Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 69; J. B. Conklin, Jr., J. E. Johnson, and G. W. Pratt, Jr., Phys. Rev. **137**, A1282 (1965).

[2] J. O. Dimmock and G. B. Wright, *Physics of Semiconductors* (Dunod Cie, Paris, 1964), p. 77.

[3] K. F. Cuff, M. R. Ellett, C. D. Kuglin, and L. R. Williams, *Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 679.

[4] K. F. Cuff, M. R. Ellett, C. D. Kuglin, and L. R. Williams (unpublished).

[5] L. Kleinman and P. J. Lin, *Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 63.

[6] M. Cardona and D. L. Greenaway, Phys. Rev. **133**, A1685 (1964).

studies extend from the infrared to 21 eV. Because of the complexities involved in the calculation of the band structure for PbTe from first principles and because of the inherent uncertainties associated with assigning observed optical structure to transitions between given symmetry points, the interpretation of the optical spectrum of PbTe has proved difficult.[1,6] For example, in their pseudopotential calculations of band structure Kleinman and Lin[5] are able to find van Hove singularities which agree well with the peaks in $\omega^2\epsilon_2$ observed by Cardona and Greenaway.[6] However, as Kleinman and Lin point out, there are many more calculated van Hove singularities than there are observed peaks in the optical spectra.

In view of the apparent complexities in the PbTe band structure and of the difficulties in interpreting the optical data, it seemed worthwhile to use another experimental tool to investigate the band structure of this material away from the band edges. Photoemission studies have proved useful in investigating a wide range of semiconductors and metals. It has been demonstrated[7–11] that much more detailed band-structure information may often be obtained by this method than by optical studies alone. Therefore, the study of photoemission from PbTe seemed profitable.

II. EXPERIMENTAL METHODS

The photoemission tubes used in this work, as well as the ac retarding potential method used for obtaining the energy distribution curves,[12] have been described previously. In order to make measurements in the vacuum ultraviolet, LiF windows were sealed to the tubes with AgCl. This limited the spectral range of measurement to photon energies less than 11.7 eV. PbTe photocathodes were formed by vacuum evaporation of PbTe from a single crystal held in a tungsten heater. PbTe was evaporated on the collector as well as the emitter to prevent a contact potential difference between emitter and collector. The evaporated layer was highly reflecting and uniform in appearance. The tube was sealed off immediately after completion of the evaporation with the final pressure less than 1×10^{-8} mm Hg. Just before the evaporation, a barium getter was fired in a remote region of the tube. Attempts were made to reduce the electron affinity by placing a monolayer of Cs or Na on the surface of the PbTe film. It was found, however, that the alkali metals reacted with the PbTe to form a distinctly different compound (as

determined by the color of the reacted chemical material).

Measurements of the spectral distribution of the photoelectric yield were made using a McPherson monochromator, Model 225, equipped with a hydrogen discharge lamp. Typically, the slits were operated at 0.5 mm, giving a band pass of about 9 Å. The light intensity was measured by a phototube coated with a sodium salicylate phosphor. The absolute value of the yield was determined at one point by comparison with a calibrated phototube.

The resolution of the energy-distribution measurements was determined by the magnitude of the ac voltage applied as well as the resolution of the monochromator. The ac voltage was 40 mV rms for $h\nu<9.5$ eV, 100 mV rms for $9.5<h\nu<11$ eV, and 200 mV rms for $h\nu>11$ eV. It is estimated that the resolution in the energy distribution measurements was 0.1 eV for $h\nu<9.5$ eV, 0.2 eV for $9.5<h\nu<11$ eV, and 0.4 eV for $h\nu>11$ eV.

The spectral distribution of the quantum yield is shown in Fig. 1. Correction has been made for the reflectivity of PbTe. The transmission correction for the LiF window was determined by measuring the transmission on similar windows. Considerable variance in the transmission was found for the spectral range above about 9 eV. Because of this variance in the transmission and of the low light intensities at high energies, the yield could not be determined as accurately above 10 eV (indicated by the dashed line in Fig. 1) as it was at lower photon energies. However, there is no doubt about the increase in yield for $h\nu>10$ eV.

III. DISCUSSION OF RESULTS

For the purpose of this discussion, it is useful to define E as the kinetic energy of the photoelectrons upon emission and E_s as the energy in the solid with respect
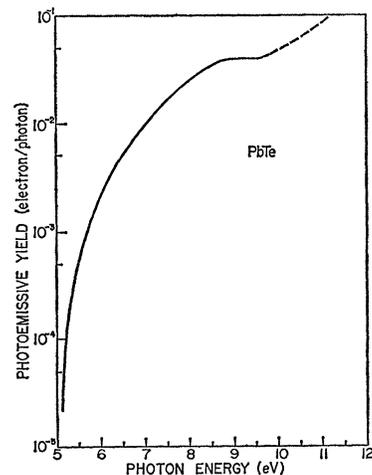
FIG. 1. The quantum yield of PbTe. The data have been corrected for the reflectivity of PbTe (Ref. 6) and for the transmission of the LiF window used.

[7] W. E. Spicer and R. E. Simon, Phys. Rev. Letters 9, 385 (1962).
[8] W. E. Spicer, Phys. Rev. Letters 11, 243 (1963).
[9] C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1030 (1964).
[10] C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1044 (1964).
[11] N. B. Kindig and W. E. Spicer (to be published).
[12] W. E. Spicer and C. N. Berglund, Rev. Sci. Instr. 35, 1665 (1964).

to the valence-band maximum. Thus, for a given value of E,

$$E_s = E + E_A + E_g, \tag{1}$$

where E_A and E_g are the electron affinity and band gap, respectively, of PbTe.

From the threshold of photoemission and the maximum energy of photoemitted electrons for monochromatic radiation, the electron affinity is estimated to be 4.6 ± 0.3 eV. For PbTe, $E_g = 0.3$ eV.

The energy distributions in Figs. 2 and 3 are plotted versus $(E - h\nu)$ rather than E. By subtracting the photon energy from the kinetic energy E of the emitted electrons, the energy distributions are referred to the initial states (valence-band states) from which the electrons are excited.[7]

Strong, well resolved structure appears in the energy distribution curves (Figs. 2, 3, and 4): (1) the doublet with maxima at $(E - h\nu)$ values of approximately -5.6 and -6.1 eV corresponding to $E_s = -0.7$ and -1.2 eV; and (2) the large maximum at $(E - h\nu) = -7.3$ eV corresponding to $E_s = -2.4$ eV. For $h\nu > 9.5$ eV, structure begins to appear in the low-energy portion of the curve. This peak never becomes completely resolved, and it is not clear whether it is due to band structure or to scattered electrons. As a result, it will not be discussed here.

When structure in the energy distribution appears at a constant value of $(E - h\nu)$ independent of $h\nu$, it must be due to structure in the valence-band density of states.[8–10] Whether the transition is direct or nondirect can be determined by such parameters as the width of structure, the range of $h\nu$ over which it maintains a constant position in energy on an $(E - h\nu)$ plot, and if it disappears, the manner in which this occurs. Evidence will be given below and in the Appendix that the doublet
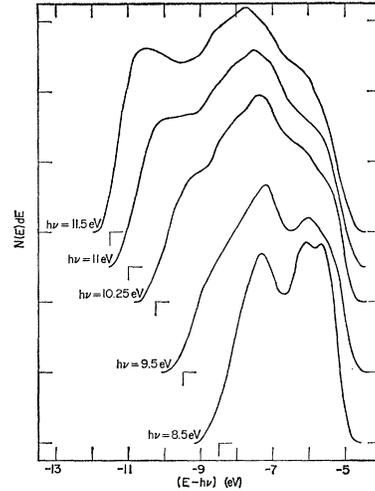
FIG. 3. Energy distribution curves obtained from PbTe plotted versus $(E - h\nu)$. E is the measured kinetic energy of the emitted electron and $h\nu$ is the energy of the exciting photons. The exciting photon energy is indicated on each curve.

is due to a direct transition whereas the structure from $E_s = -2.4$ eV is probably due to a nondirect transition.

From Figs. 2, 3, and 4 it can be seen that there must be the following strong structure in the valence band of PbTe: (1) a doublet with maxima located approximately 0.7 and 1.2 eV below the valence-band maximum; and (2) strong structure located 2.4 eV below the valence-band maximum.

The doublet disappears abruptly as the photon energy is increased from 9 to 10 eV. This can be seen in Figs. 2, 3, and 4. The disappearance of this doublet might be due to either electron-electron scattering[9,10] or to the disappearance of the final (conduction) band involved in a direct transition. The abruptness with which the doublet disappears suggests that the disappearance is not due to electron-electron scattering but to conduction-band structure and that the transition is direct.

It is important to note that the higher energy member of the doublet disappears first and then its partner dis-

FIG. 2. Energy distribution curves obtained from PbTe plotted versus $(E - h\nu)$. E is the measured kinetic energy of the emitted electron and $h\nu$ is the energy of the exciting photons. The exciting photon energy is indicated on each curve.
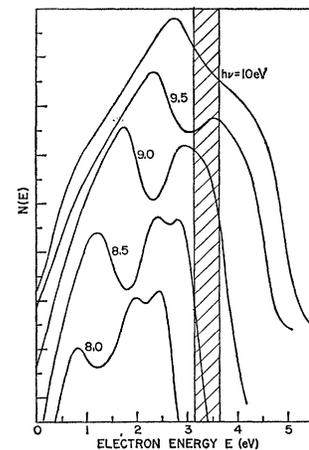
FIG. 4. Energy distributions for 8.0 eV $< h\nu < 10.0$ eV plotted versus E. The region between 3.25 and 3.75 eV has been cross hatched to emphasize the fact that the doublet disappears in this energy range.
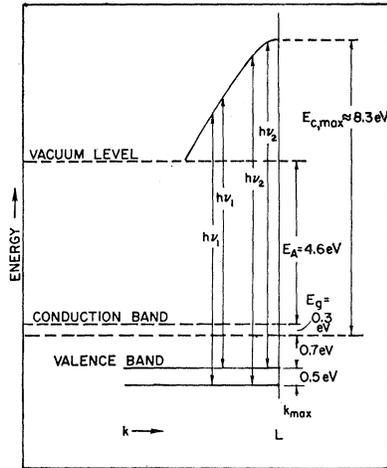
FIG. 5. Features of the band structure near the L point as deduced from this work.

TABLE I. The location of PbTe symmetry points at L by various works. The zero of energy has been taken at the valence-band maximum.

| | Symmetry points | | |
	L_4^+, $L_5^+(L_3)$ (eV)	$L_6^+(L_3)$ (eV)	L_6^- and/or L_5^-, $L_4^-(L_3')$ (eV)
Conklin, Johnson, and Pratt (Ref. 1)	-0.86	-1.33	0.93, 1.53
Kleinman and Lin (Ref. 5)	-0.75	-1.38	1.06, 1.66
Cuff et al. (Ref. 4)	-0.8	-1.4	1.2
This work	-0.7	-1.2	1.3

appears as it moves through approximately the same final energy. Since the final energy is given by E (see Eq. 1), this can be seen most easily in Fig. 4 where the energy distributions for $8 < h\nu < 10$ eV have been plotted versus E. The approximate range in final energy over which the structure disappears is indicated by the cross-hatched area in Fig. 4. Thus the manner in which the doublet disappears suggests that the conduction band involved in the excitation disappears at $3.2 < E < 3.7$ eV, i.e., $8.1 < E_s < 8.6$ eV.

The disappearance of the strong transition due to the doublet could produce the plateau which appears in the yield curve (Fig. 1) for $8.7 < h\nu < 9.8$ eV. For $h\nu < 8.7$ eV, the yield increases monotonically with $h\nu$ due to the increased number of valence-band states from which photoelectrons can be excited and to the fact that no strong transitions are disappearing. For $8.7 < h\nu < 9.8$ eV, a plateau appears since the loss due to the disappearance of the doublet is approximately equal to the increase due to the uncovering of new valence-band states.

The features of band structure which are consistent with the experimental data under discussion are indicated in Fig. 5. There are assumed to be two relatively flat valence bands located near k_{max}, approximately 0.7 and 1.2 eV below the valence-band maximum. The direct optical transitions observed in the photoemission experiment are those due to a conduction band which has the following features: (1) a much larger slope than the valence bands from which the electrons are excited; and (2) a maximum at L approximately 8.3 eV (i.e., between 8.1 and 8.6 eV) above the lowest conduction-band state. Because the conduction-band slope is much greater than those of the valence bands, the energy of the maxima in $N(E)$ due to excitation from the valence band is given by $E = h\nu - E_0$, where E_0 is the initial energy. These maxima disappear at an electron kinetic energy of approximately 3.4 eV ($E_s = 8.3$ eV) due to the termination of the conduction band. In the recent calculations of Conklin, Johnson, and Pratt,[1] the conduc-

tion bands extending from Γ_8^+ to (L_4^-, L_5^-), L_6^-, and L_6^- have the general character and position of the conduction band shown in Fig. 5. The increase in strength of each peak just before its disappearance might be a reflection of complex structure near L.

It is important to note that the large maximum which appears in the $(E - h\nu)$ energy distribution plots at 2.4 eV *does not* disappear as it moves through the conduction-band states at which the doublet disappears (see Fig. 3). This is further evidence that the disappearance of the doublet is not due to electron-electron scattering. It also suggests that the 2.4 eV structure is not due principally to transitions to the conduction band associated with the doublet; thus, that the 2.4-eV structure is associated with different regions of k space than the doublet structure and, as is discussed in the Appendix, it is due principally to nondirect transitions.[8–10]

Since the valence-band maximum in PbTe occurs at the L point, it is likely that the 0.7 and 1.2 eV structure also lies near that point.[1] The position of structure at the L point as predicted from band calculations by Conklin, Johnson, and Pratt[1] and by Kleinman and Lin,[2] and as deduced from experimental and theoretical work by Cuff et al.,[3] is shown in Table I. As can be seen, the values obtained here are in reasonable agreement with the previous determinations. It should be emphasized that the results presented here are the first *direct* experimental observations of this structure.

It is useful to compare the results obtained here with the optical data of Cardona and Greenaway.[6] Cardona and Greenaway observed structure in the optical data at photon energies of approximately 1.25 and 2.2 eV. Since the peak-to-valley ratio for the doublet structure observed here is not strong (the peak-to-valley ratio was only about 1.04), it would be quite difficult to resolve the two peaks in optical measurements. It is suggested that the optical peak at 1.25 eV is due to excitation from the valence bands at $E_s = -0.7$ and -1.2 eV to the conduction-band minimum. The energy of this transition would be between 1.0 eV (1st peak) and 1.5 eV (2nd peak) as compared to the measured value of 1.25 eV. It is interesting to note that in Cardona and Greenaway's n and k curves for PbTe, faint structure does appear at approximately 1.6 eV. If the large optical peak at 2.2 eV is also assigned to transitions from the

doublet, this would locate the next highest conduction-band structure approximately 1.3 eV above the valence-band maximum. As can be seen from Table I, this is in reasonable agreement with the predicted values.

The optical transition involving the doublet observed in photoemission here may be responsible for the peak in the reflectivity at 7.8 eV reported by Cardona and Greenaway. Examination of Figs. 2 through 4 shows that each member of the doublet reaches a maximum in relative magnitude at $E=2.4$ eV $(E_s=7.3)$. Thus a maximum in optical data would be expected near 8 eV.

IV. CONCLUSIONS

A doublet has been observed in the energy distribution of photoelectrons due to energy bands lying 0.7 and 1.2 eV below the valence-band maximum. This structure is associated with relatively flat bands lying near the L point and associated with the L_3^{45} and L_3^6 bands. The photoemission results are in reasonable agreement with the energy-band determinations of these points by Kleinman and Lin,[5] Conklin, Johnson, and Pratt,[1] and Cuff et al.[4] Using the photoemission data and Cardona and Greenaway's[6] optical data, it is deduced that a second conduction band is located approximately 1.3 eV above the valence-band maximum near the L point, in general agreement with the values suggested by other workers. Evidence is found for a conduction band which terminates approximately 8.3 eV above the valence-band maximum. Strong structure is located in the valence band 2.4 eV below the valence-band maximum. This structure is associated principally with regions in $\mathbf{k}$ space other than those near the L point and with nondirect transitions.[7]

APPENDIX: DIRECT AND NONDIRECT TRANSITIONS IN PbTe

It was pointed out in Sec. IVA of Ref. 9 that optical transitions from a band in which E is almost independent of $\mathbf{k}$ will provide a maximum in energy distributions which are found at a constant energy on an $(E-h\nu)$ plot independently of whether the optical transition is direct or nondirect. However, if the transition is direct, the flat band will couple to only those conduction-band states having identical values of $\mathbf{k}$. Thus, if the conduction band to which a direct transition is being made terminates, the structure associated with this particular transition must disappear. However, if the transition is nondirect, it is necessary that there be *no* states *anywhere* in $\mathbf{k}$ space at a given energy for the transition to disappear at that energy due to band structure. In other words, structure due to nondirect transition will not disappear unless a true forbidden zone occurs in the conduction band.

In PbTe, band calculations[1-5] indicate that the valence bands near (L_4^+,L_5^+) and L_6^+ are relatively flat. As a result, it is not surprising that electrons excited from them appear at a constant energy on an $(E-h\nu)$ plot over a range of approximately 3.5 eV.[12] The direct nature of the doublet transition is established by the manner in which the doublet disappears. The doublet structure disappears abruptly (within an energy range of 0.5 eV) near a given value of final (conduction) band energy $(E_s=8.3$ eV), whereas the structure due to excitation from $E_s=-2.4$ eV does not disappear as it moves through the same range of energy. This behavior can only be explained if the selection rules for $E_s \gtrsim 8.3$ eV are quite different for the doublet transition and for the transitions from $E_s=-2.4$ eV. The only selection rule which would be expected to be sufficiently strong to explain this marked difference is conservation of $\mathbf{k}$.

The width of each peak making up the doublet (a few tenths of an eV) is consistent with this explanation. The fact that the structure peaked around excitations from $E_s=-2.4$ eV is quite wide (over an electron volt) and is found at approximately a constant energy on an $(E-h\nu)$ plot *suggests* that this is due to nondirect transitions. However, the range in energy over which this peak can be followed[13] is too small for any definite statement to be made as to whether it is direct or nondirect. If it is direct, the present data indicate that it is associated with states in a different position in $\mathbf{k}$ space from the doublet.

It is interesting to compare the behavior of the doublet in PbTe with the peak in the energy distributions in Cu due to excitation from highest lying flat-band d band in Cu (see Sec. IVA of Ref. 9 and Sec. II of Ref. 10). This peak can be followed in photoemission over an energy range of 5.0 eV; however, it broadens and decreases in peak strength monotonically as the energy increases. For $h\nu > 9.5$ eV, it can no longer be resolved. Since this behavior was consistent with the scattering effects observed in Cu, the broadening and disappearance of this peak have been attributed to scattering. This is to be contrasted to the abrupt disappearance of the doublet in PbTe where the peaks become *sharper* just before they disappear and where the peak due to excitation from $E_s=-2.4$ eV does not show any sudden scattering loss as it moves through $E_s=8.3$ eV.

In conclusion, it should be stated that the fact that the behavior of the doublet in PbTe can be explained in terms of direct transitions does not invalidate earlier evidence for nondirect transitions.

[13] In cases where nondirect transitions have been reported, the range usually has extended over the complete range of observation. For example, this was 7 eV or greater in the I-V compounds (Refs. 8, 14) and for the principal d-band peak in Cu.

[14] W. E. Spicer, J. P. Hernandez, and F. Wooten, Bull. Am. Phys. Soc. 8, 614 (1963).