polaron ($\alpha \ll 1$) in a Coulomb field was calculated for the case $\beta = (E_B/\omega_0)^{1/2} \ll 1$ by the method of Platzman. The disagreement between the correction to the binding energy as determined by Platzman and the result of an effective-mass equation with corrections to the orders $\alpha\beta^2\omega_0$ and $\alpha\beta^4\omega_0$ is removed if Platzman's procedure is improved by adding one step in his iterative process. The binding energy is given by the expression (25). The method of expanding the energy in powers of β cannot be extended in a simple way to include corrections of the orders beyond β^4.

ACKNOWLEDGMENTS

I thank Dr. David Larsen for a discussion which stimulated this work. I also thank Professor M. H. Cohen and Dr. S. Kirkpatrick for reading the manuscript.

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*Work supported by NASA and Advanced Research Projects Adminstration.

[1] H. Fröhlich, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield, (Plenum, New York, 1963).

[2] P. M. Platzman, Phys. Rev. 125, 1961 (1962).

[3] The sign of the $\alpha\beta^4\omega_0$ term in Eq. (3) is in error in Platzman's paper as has been pointed out by Larsen (Ref. 4).

[4] D. M. Larsen, Phys. Rev. 187, 1147 (1969).

[5] J. Sak, Phys. Status Solidi 27, 521 (1968).

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Energy-Gap Anomaly in the Semiconductor Sequence PbS, PbSe, and PbTe

Richard Dalven*
Department of Physics, University of California, Berkeley, California 94720

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The *f*-sum rule has been examined at the conduction- and valence-band edges of PbS, PbSe, and PbTe. Experimental values of electron and hole effective masses, and of energy gaps were used. For both two-band and six-band models, it was found that PbTe *does not* follow the same *f*-sum rule as do PbS and PbSe. However, it was also found that, for the III-V and II-VI semiconductor sequences (InSb, InAs, InP), (GaSb, GaAs), and [CdSe, CdS (hexagonal)], the members of each sequence *do* follow the same *f*-sum rule. It is concluded that the well-known anomaly in the values of the energy gap E_G of the Pb*X* sequence $[E_G(\text{PbS}) > E_G(\text{PbTe}) > E_G(\text{PbSe})]$ is due to an irregular value of E_G for PbTe. It appears likely that this anomalous value of the energy gap of PbTe reflects, through the L_6^- conduction-band edge, an irregular value of the 5*s* electron energy of the tellurium atom. It is proposed that the L_6^- conduction-band edge states in PbTe differ from the equivalent states in PbS and PbSe. This difference results in PbTe having an *f*-sum matrix element different from that for PbS and PbSe; this is the reason that PbTe does not follow the same *f*-sum rule as do PbS and PbSe. The *f*-sum-rule plots of the experimental data for these semiconductors have been used to calculate matrix element values.

I. INTRODUCTION

The energy gap E_G of a compound semiconductor *MX* is generally observed to decrease as the atomic number of the atom *X* increases. Examples of this well-known "rule" may be observed by considering the energy-gap values given in Table I for several series of semiconductors. The values shown are optically determined values of E_G for two III-V series and two II-VI series, including both zinc-blende and wurtzite structures. For each series, the energy gap of *MX* decreases monotonically as the atomic number of atom *X* increases. The data shown, covering different crystal structures and a range of energy gap of more than a factor of 10, demonstrate that this rule is well established experimentally.

However, the energy gaps of PbS, PbSe, and PbTe *do not* exhibit this monotonic decrease. The experimental values[1,2] of E_G between 4 and 373 °K for these semiconductors are such that $E_G(\text{PbS}) > E_G(\text{PbTe}) > E_G(\text{PbSe})$. Precise values[1] of these energy gaps at 4 °K are: for PbS, $E_G = (0.286 \pm 0.003)$ eV; for PbTe, $E_G = (0.190 \pm 0.002)$ eV; for PbSe, $E_G = (0.165 \pm 0.005)$ eV. The fact that the sequence of energy-gap values for the PbS group is anomalous in that $E_G(\text{PbSe}) < E_G(\text{PbTe})$ has been noted by a number of authors[3-6] as far back as 1959. However, there appears to have been little explicit discussion of which member or members of the sequence exhibit an irregular value of the energy gap, and thus even less discussion of possible reasons for the existence of this irregularity.

This paper is a theoretical study, previously reported[7] in preliminary form as a letter, whose aims were: (a) a determination of the irregular member(s) of the PbS sequence; (b) obtaining information concerning the reasons for the existence

TABLE I. Values of the energy gap E_G (in eV) for several III-V and II-VI compound semiconductors.

	T (°K)	E_G (eV)	Ref.		T (°K)	E_G (eV)	Ref.
InP	4	1.416	a				
InAs	4	0.425	a	GaAs	4	1.517	a
InSb	4	0.236	a	GaSb	4	0.813	a
ZnS[c]	298	3.66 – 3.76	d	CdS[e]	298	2.53; 2.53[b]	d
ZnSe[c]	297	2.67	f	CdSe[e]	298	1.9; 1.85[b]	d
ZnTe[c]	300	2.25	g	CdTe[e]	• • •	h	

[a] These data are from O. Madelung, *Physics of III-V Semiconductors* (Wiley, New York, 1964), p. 352, where full references to the original work will be found. (GaP is omitted because its conduction-band structure differs from that of GaAs and GaSb.)

[b] Values determined using radiation polarized $\vec{E} \parallel c$ and $\vec{E} \perp c$, respectively.

[c] Cubic (zinc-blende) structure.

[d] M. Cardona and G. Harbeke, Phys. Rev. 137, A1467 (1965).

[e] Hexagonal (wurtzite) structure.

[f] M. Cardona, J. Appl. Phys. Suppl. 32, 2151 (1961).

[g] R. E. Nahory and H. Y. Fan, Phys. Rev. 156, 825 (1967).

[h] Data not available.

of the irregularity.

II. THEORY

In order to investigate the energy-gap sequence in the lead-compound semiconductors, the f-sum rule[8] was used. For the L point of the Brillouin zone of the fcc lattice, the f-sum rule may be written as

$$\left(\frac{m}{m^*}\right)_{ij} = \delta_{ij} + \frac{2}{m} \sum_{n}{}' \frac{\langle p, L | \pi_i | L, n\rangle \langle n, L | \pi_j | L, p\rangle}{E_{p,L} - E_{n,L}} . \tag{1}$$

In Eq. (1), $(m/m^*)_{ij}$ is the ijth component of the effective-mass tensor at the point $k = L$ of the band p, the symbol δ_{ij} is the Kronecker delta, and m is the free-electron mass. In the matrix elements, p and n are band indices, L represents the L point, and π_j is the jth component of the quantity $\vec{\pi}$ defined[9] by $\vec{\pi} \cdot \vec{k} = mH'$, where H' is the perturbation used in $\vec{k} \cdot \vec{p}$ theory. The quantities $E_{p,L}$ and $E_{n,L}$ are the energies of the bands p and n, respectively, at the L point. The summation in Eq. (1) is taken over all bands n ($n \neq p$) which interact with band p. The unperturbed Hamiltonian is the Hamiltonian for $\vec{k} = L$.

For PbS, PbSe, and PbTe, the surfaces of constant energy are prolate ellipsoids of revolution for both holes and electrons. These surfaces are characterized by two effective masses, a longitudinal effective mass m_l and a transverse effective mass m_t. The longitudinal axis of the constant-energy surface is the $\langle 111 \rangle$ direction in $\vec{k}$ space. Since a transverse cross section of the constant-energy surface is a circle, there are no off-diagonal terms in the effective-mass tensor, and $i = j$ for both m_t and m_l. Thus Eq. (1) contains only terms for which $i = j$, and the matrix element product in the sum in Eq. (1) may be written[10] as $|\langle n, L | \pi_j | L, p\rangle|^2$.

We now consider band structures of the lead-compound semiconductors to which the f-sum rule may be applied. The simplest model is one comprised of only two bands. The band p is the lowest conduction band (L_6^-) and the band n is the highest valence band (L_6^+). These two bands thus define the energy gap, and in the notation of Eq. (1), $E_{p,L} = E(L_6^-)$, $E_{n,L} = E(L_6^+)$, and the energy gap $E_G = E(L_6^-) - E(L_6^+)$. The sum in the f-sum rule contains only one term in this case and Eq. (1) reduces to $m/m^* = 1 + (2/m)(|M|^2/E_G)$, where m^* is either m_l or m_t, and M is either $\langle n, L | \pi_l | p, L\rangle$ or $\langle n, L | \pi_t | p, L\rangle$. Rearrangement gives

$$m^*/(m - m^*) = (\tfrac{1}{2} m / |M|^2) E_G . \tag{2}$$

Equation (2) shows that, for this simple two-band model, $m^*/(m - m^*)$ is proportional to the energy gap E_G. Moreover, the linear plot of $m^*/(m - m^*)$ as a function of E_G passes through the origin, i.e., the point $[m^*/(m - m^*) = 0,\ E_G = 0]$.

In a more realistic band picture, additional bands of index n interacting with the band p under consideration should be included in the sum in Eq. (1). Recently, Herman and his co-workers have reported[11] calculated band structures of PbS, PbSe, and PbTe. From their results, the appropriate bands in the f sum are (in order of decreasing energy) as follows: L_{45}^-, L_6^-, L_6^- (lowest conduction band), L_6^+ (highest valence band), L_{45}^+, L_6^+, all in double-group notation. Thus the more realistic f sum will contain five terms due to six bands and is of the form

$$m^*/(m - m^*) = (\tfrac{1}{2} m / |N|^2) \sigma , \tag{3}$$

where m^* is again either m_l or m_t. In Eq. (3), which is the multiband analog of Eq. (2), the same value $|N|$ was assumed for each of the matrix elements in the f-sum rule; the quantity σ is then defined by the equation

$$\sigma^{-1} \equiv \textstyle\sum_n' (E_{p,L} - E_{n,L})^{-1} .$$

Thus, given the energy differences $(E_{p,L} - E_{n,L})$ for the bands involved, and subject to the approximation that each matrix element in the f sum has the same magnitude $|N|$, a plot of $m^*/(m - m^*)$ as a function of σ should be a straight line passing through the origin $[m^*/(m - m^*) = 0,\ \sigma = 0]$.

We may also examine the two-band f-sum rule at the band edges of additional semiconductors with different crystal structures. In particular, InSb,

TABLE II. Data on effective masses for PbS, PbSe, and PbTe at 4 °K (m is the free-electron mass).

Compound	Carrier	(m_t/m)	$m_t/(m-m_t)$	(m_l/m)	$m_l/(m-m_l)$	Ref.
PbS	Electrons	0.080 ± 0.01	0.087 ± 0.012	0.105 ± 0.015	0.117 ± 0.019	a
PbS	Holes	0.075 ± 0.01	0.081 ± 0.012	0.105 ± 0.015	0.117 ± 0.019	a
PbSe	Electrons	0.040 ± 0.008	0.042 ± 0.009	0.07 ± 0.015	0.075 ± 0.018	a
PbSe	Holes	0.034 ± 0.007	0.035 ± 0.007	0.068 ± 0.015	0.073 ± 0.017	a
PbTe	Electrons	0.024 ± 0.003	0.025 ± 0.003	0.24 ± 0.05	0.316 ± 0.082	a
PbTe	Holes	0.022 ± 0.003	0.023 ± 0.004	0.31 ± 0.05	0.45 ± 0.11	a
PbTe	Holes	0.036 ± 0.002	0.037 ± 0.002			b

[a] K. F. Cuff, M. R. Ellett, C. D. Kuglin, and L. R. Williams, in *Physics of Semiconductors: Proceedings of the Seventh International Conference, Paris*, 1964, edited by M. Hulin (Academic, New York, 1964), p. 677; the calculations of $m^*/(m-m^*)$ were made from these data by the author.

[b] J. R. Burke, B. Houston, and H. T. Savage, Phys. Rev. (to be published).

InAs, InP, GaSb, GaAs, and hexagonal CdS and CdSe were investigated. All of these semiconductors have both their conduction- and valence-band edges at the Γ point.[12] The constant-energy surfaces[13] for electrons (Γ_6 band) in these III-V semiconductors are spheres; for light (Γ_8 band) holes, the constant-energy surfaces are warped spheres. For hexagonal CdS and CdSe, the electron (Γ_7 band) constant-energy surfaces[14,15] are spheres within experimental error; for holes (Γ_9 band) the constant-energy surfaces are spheroidal.[13] For both spherical and spheroidal constant-energy surfaces, there are no off-diagonal terms in the effective-mass tensor. Then $i=j$ in Eq. (1) (evaluated at $\vec{k}=\Gamma$), and Eq. (2) is applicable. This is the case for electrons in the III-V compounds listed above and for electrons and holes in hexagonal CdS and CdSe. If the warping and consequent deviation from sphericity of the III-V light-hole constant-energy surfaces is small, then Eq. (2) would be approximately satisfied for these light holes also. Then, applying the two-band model to these III-V and II-VI semiconductors, we expect values of $m^*/(m-m^*)$ for electrons and holes plotted as a function of energy gap E_G to be straight lines passing through the point $[m^*/(m-m^*)=0,\ E_G=0]$.

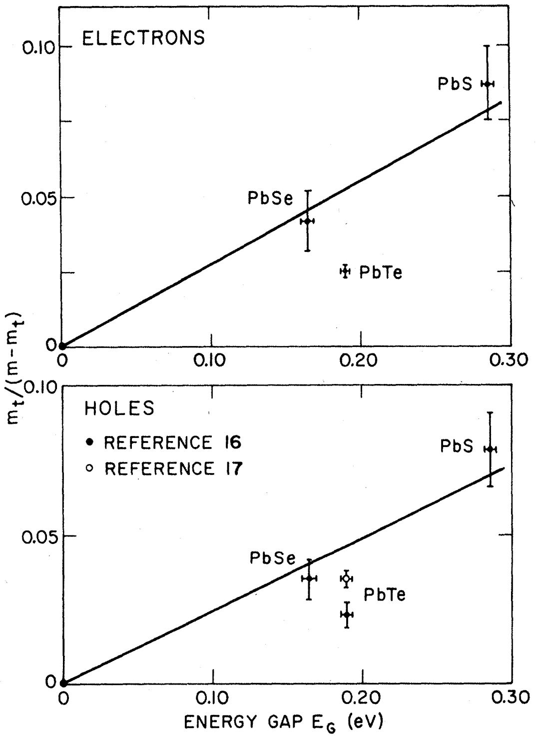

FIG. 1. $m_t/(m-m_t)$ as a function of energy gap E_G for electrons and holes.

III. RESULTS

In order to investigate the sequence of energy gaps in PbS, PbSe, and PbTe, the f-sum rule was applied to experimental values of the energy gap E_G and the effective masses m_l and m_t. The values of energy gap used are quoted[1] above. The longitudinal and transverse effective masses m_l and

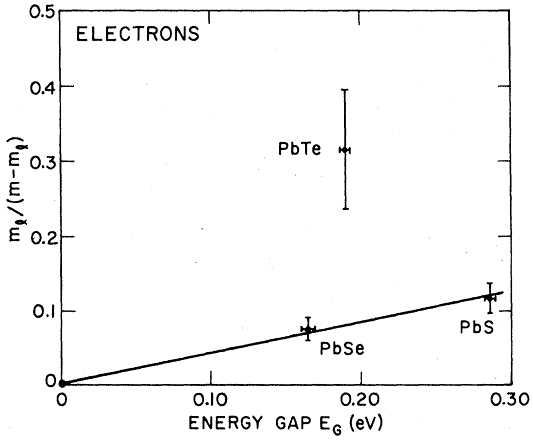

FIG. 2. $m_l/(m-m_l)$ as a function of energy gap E_G for electrons.

TABLE III. Energy differences (in eV) defining σ.

$E_{p,L} - E_{n,L}$	PbS	PbSe	PbTe
$E(L_6^-) - E(L_{45}^-)$	-2.67	-2.37	-1.70
$E(L_6^-) - E(L_6^-)$	-1.76	-1.54	-1.20
$E(L_6^-) - E(L_6^+)$	0.286	0.165	0.190
$E(L_6^-) - E(L_{45}^+)$	2.56	2.08	1.20
$E(L_6^-) - E(L_6^+)$	2.60	2.19	1.78
$E(L_6^+) - E(L_{45}^-)$	-2.91	-2.70	-1.85
$E(L_6^+) - E(L_6^-)$	-2.00	-1.87	-1.45
$E(L_6^+) - E(L_6^-)$	-0.286	-0.165	-0.190
$E(L_6^+) - E(L_{45}^+)$	2.52	1.86	0.95
$E(L_6^+) - E(L_6^+)$	2.36	2.08	1.53

TABLE IV. Calculated values of σ (eV).

Band p	PbS	PbSe	PbTe
L_6^-	0.300	0.153	0.191
L_6^+	-0.282	-0.152	-0.208

m_t are those reported by Cuff and co-workers[16] as determined by de Haas–Shubnikov measurements at 4.2 °K. These data are given in Table II, as is a very recent value[17] of m_t, at approximately 4 °K, for holes at the Fermi surface in p-type PbTe containing 3.0×10^{18} holes cm^{-3}. Figures 1–3 show plots of $m^*/(m - m^*)$ as a function of the energy gap E_G for $m^* = m_l$ and $m^* = m_t$ for both holes and electrons. In each plot, it is clearly apparent that, within the experimental errors shown, the points for PbS, PbSe, and the origin define a good straight line, whereas the point for PbTe does *not* lie on this line. The semiconductors PbS and PbSe satisfy the same two-band f-sum rule, whereas PbTe does not. It is also noteworthy that, for the plots of longitudinal effective mass for both electrons and holes, the point for PbTe lies *above* the straight line defined by the points for PbS, PbSe, and the origin.

To investigate the situation when additional bands

TABLE V. Effective-mass and energy-gap data for several III-V and II-VI semiconductors (m is the free-electron mass).

Compound	T (°K)	Carrier	Ref.	m^*/m	$m^*/(m - m^*)$	E_G (eV)	Ref.
InSb	80	Electrons	a	0.0145 ± 0.0005	0.0147 ± 0.0005	0.225	b
InAs	80	Electrons	c, d	0.024 ± 0.002	0.025 ± 0.002	0.41	b
InP	80	Electrons	c	0.077 ± 0.005	0.084 ± 0.006	1.41	b
GaAs	80	Electrons	a, e	0.073 ± 0.005	0.079 ± 0.006	1.51	b
GaSb	80	Electrons	f	0.049 ± 0.005	0.052 ± 0.006	0.80	b
InSb	20	Light holes	g	0.0160 ± 0.0006	0.0163 ± 0.0007	0.2355	h
InAs	20	Light holes	h	0.026 ± 0.002	0.027 ± 0.002	0.41	i
GaAs [h']	•••	Light holes	i	0.12 ± 0.03	0.136 ± 0.04	1.52	b
GaSb	20	Light holes	j	0.052 ± 0.005	0.055 ± 0.005	0.81	b
CdS	4	Electrons	k	0.204 ± 0.010	0.258 ± 0.015	2.582	l
CdSe	1.8	Electrons	m	0.13 ± 0.02	0.15 ± 0.025	1.840	l
CdS	4	Perpendicular holes	k	0.7 ± 0.1	$2.34 \left\{\begin{matrix} +1.63 \\ -0.84 \end{matrix}\right.$	2.582	l
CdSe	1.8	Perpendicular holes	m	0.45 ± 0.09	$0.82 \left\{\begin{matrix} +0.35 \\ -0.31 \end{matrix}\right.$	1.840	l

[a] E. D. Palik, S. Teitler, and R. F. Wallis, J. Appl. Phys. Suppl. 32, 2132 (1961).

[b] D. Long, *Energy Bands in Semiconductors* (Wiley, New York, 1968), p. 111.

[c] E. D. Palik and R. F. Wallis, Phys. Rev. 123, 131 (1961).

[d] E. D. Palik and J. R. Stevenson, Phys. Rev. 130, 1344 (1963).

[e] E. D. Palik, J. R. Stevenson, and R. F. Wallis, Phys. Rev. 124, 701 (1961).

[f] H. Piller, J. Phys. Chem. Solids 24, 425 (1963).

[g] C. R. Pidgeon and R. N. Brown, Phys. Rev. 146, 575 (1966).

[h] C. R. Pidgeon, D. L. Mitchell, and R. N. Brown, Phys. Rev. 154, 737 (1967).

[h'] *Footnote added in proof.* A very recent experimental value of the light-hole effective mass in GaAs has been reported by A. L. Mears and R. A. Stradling [J. Phys. C 4, L22 (1971)]. Their value is $m^* = (0.087 \pm 0.005)m$ at 50 °K, leading to a value of $m^*/(m - m^*) = 0.096 \pm 0.006$. This new value of $m^*/(m - m^*)$ for GaAs is an even better fit to the straight line in Fig. 8 than is the point shown.

[i] H. Ehrenreich, Phys. Rev. 120, 1951 (1960). In this paper, the author estimates the light-hole effective mass in GaAs at low temperatures, and he suggests an approximate accuracy of 30%.

[j] R. A. Stradling, Phys. Letters 20, 217 (1966).

[k] J. J. Hopfield and D. G. Thomas, Phys. Rev. 122, 35 (1961).

[l] D. Long, *Energy Bands in Semiconductors* (Wiley, New York, 1968), p. 133.

[m] R. G. Wheeler and J. O. Dimmock, Phys. Rev. 125, 1805 (1962).

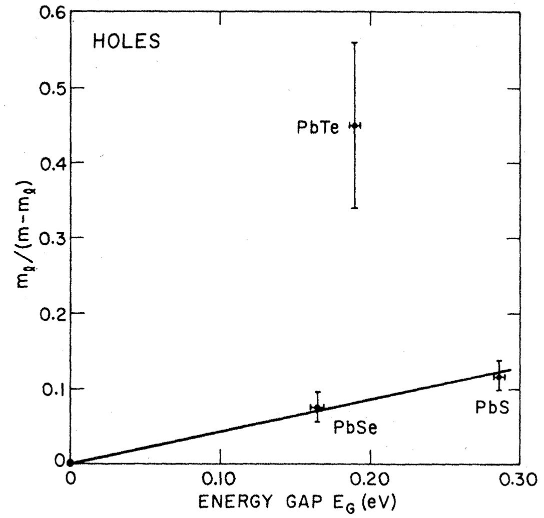

FIG. 3. $m_l/(m-m_l)$ as a function of energy gap E_G for holes.

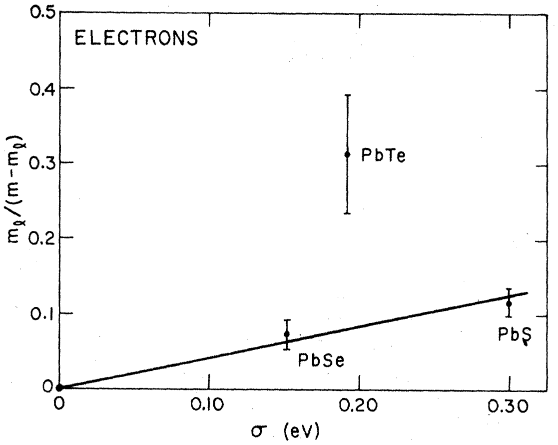

FIG. 5. $m_l/(m-m_l)$ as a function of σ for electrons.

are included, the f sum in Eq. (1) was carried out including five bands (of index n) for the cases in which the band p under consideration was: (a) the lowest conduction band L_6^-; and (b) the highest valence band L_6^+. The former case would lead to Eq. (3) for electron masses, the latter to Eq. (3) for hole masses. The energy separations $(E_{p,L} - E_{n,L})$ were taken [except for experimental values of $E_G = E(L_6^-) - E(L_6^+)$] from the calculated results of Herman *et al.*[18]; these are shown in Table III for the six bands considered. Using these energy differences, the quantity σ was calculated and the results are shown in Table IV. Since, for holes (i.e., band $p = L_6^+$, the highest valence band) $\sigma < 0$ when calculated from the energy separations in Table III, values of $-\sigma$ were used in making these f-sum-rule plots for holes. Following Eq. (3), plots of $m^*/(m-m^*)$ as a function of the calculated values of σ or $-\sigma$ are shown in Figs. 4–6 for $m^* = m_t$ and $m^* = m_l$. As in the plots for the two-band model, it is apparent that the points for PbS and PbSe and the origin $[m^*/(m-m^*) = 0,\ \sigma = 0]$ form a good straight line upon which the point for PbTe does *not* fall. The general form of the plots is the same for the six-band model as for the two-band

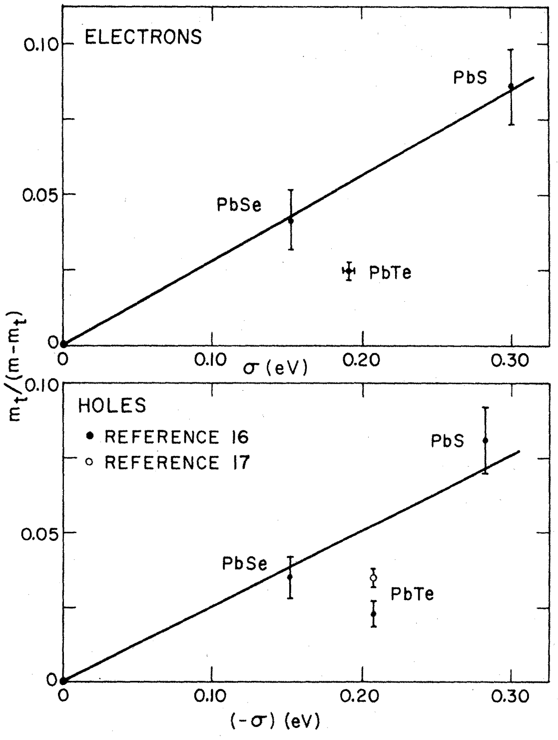

FIG. 4. $m_t/(m-m_t)$ as a function of σ and $-\sigma$ for electrons and holes, respectively.

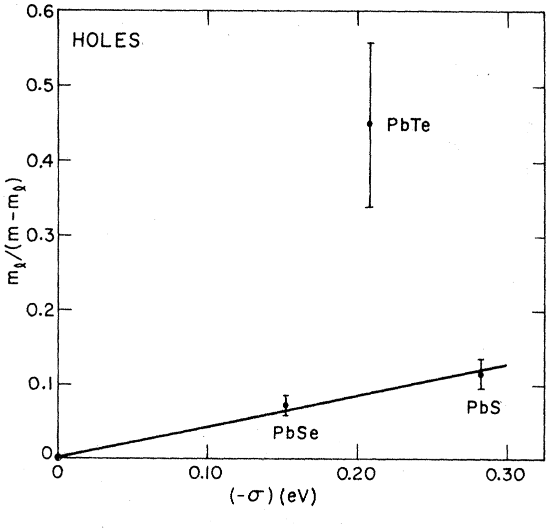

FIG. 6. $m_l/(m-m_l)$ as a function of $-\sigma$ for holes.

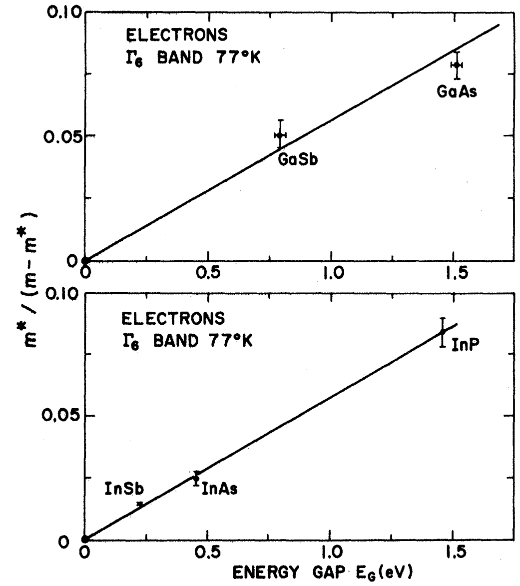

FIG. 7. $m^*/(m-m^*)$ as a function of energy gap E_G for electrons. The temperature shown is that at which the experimental data were taken.

model. As might be expected, the fit of the straight line to the points for PbS and PbSe is somewhat better in the six-band case.

Similar plots of $m^*/(m-m^*)$, for electrons and light holes, as a function of energy gap E_G have been made for the sequences (InSb, InAs, InP) and (GaSb, GaAs),[19] and for electrons and perpendicular holes in hexagonal CdS and CdSe. The effective-mass data used are shown in Table V, as are the appropriate values of the energy gaps. The results[20] are shown in Figs. 7–9. In each case, the points shown lie, within the experimental error of the data, on a good straight line passing through the origin, i.e., the point $[m^*/(m-m^*)=0,\ E_G=0]$.

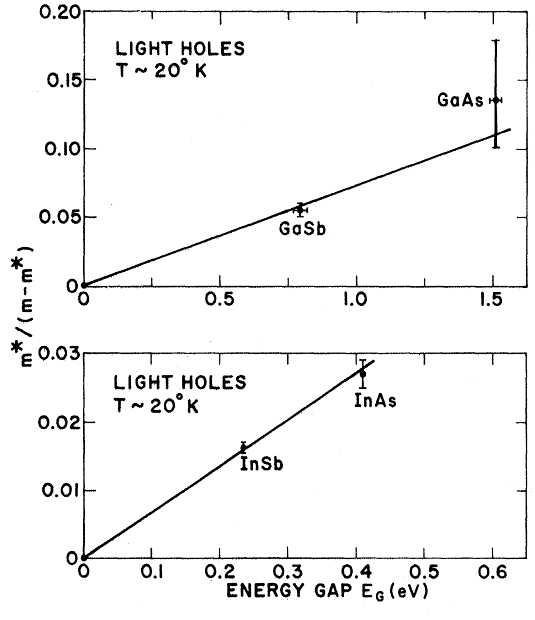

FIG. 8. $m^*/(m-m^*)$ as a function of energy gap E_G for light holes. The temperature shown is that at which the experimental data were taken.

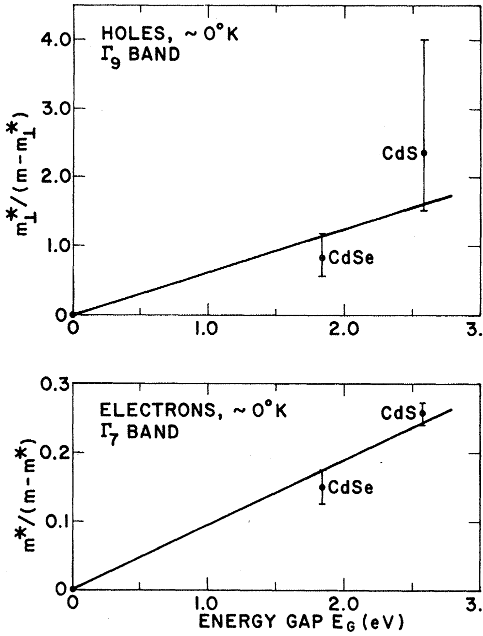

FIG. 9. $m_\perp^*/(m-m_\perp^*)$ for light holes, and $m^*/(m-m^*)$ for electrons as a function of energy gap E_G. The temperature shown is that at which the experimental data were taken.

IV. DISCUSSION

The principal results embodied in Figs. 1–9 are: (a) for the three semiconductor sequences InX, GaX, and CdX, the experimental data for each sequence follow the same f-sum rule, and the f-sum matrix element is thus the same for all of the members of a given sequence; (b) for the PbX sequence, the data for PbTe *do not* follow the same f-sum rule as do the data for PbS and PbSe. In addition, the indium-, gallium-, and cadmium-compound semiconductors all show a series of energy-gap values which decreases monotonically as the atomic number of atom X increases. It is therefore concluded that the irregular member of the PbS-PbSe-PbTe sequence is the one, namely, PbTe, which does not satisfy the same f-sum rule followed by the other members of the sequence. It is thus proposed that the irregular value of the energy gap in the PbX sequence is that of PbTe. Further, it is suggested that this irregularity is due only to an anomalously large value of the energy gap for PbTe, rather than to an anomalously low

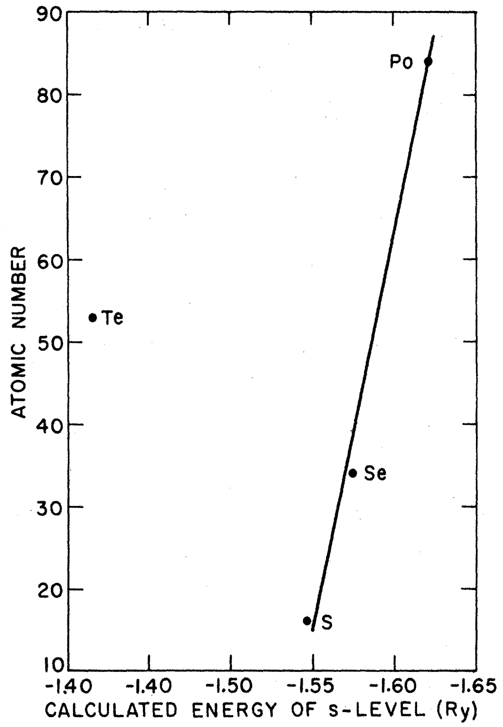

FIG. 10. Calculated s-level energy as a function of atomic number for S, Se, Te, and Po.

value for PbSe.[21]

The plots of longitudinal effective masses m_l, shown in Figs. 2, 3, and 5, are especially interesting. In every case, the point for PbTe lies *above* the f-sum line satisfied by PbS and PbSe. There is, then, no way in which the point for PbTe on the m_l plots can lie on this line while having, simultaneously, the observed values of m_l and a value of energy gap less than the energy gaps of PbS and PbSe. This observation suggests that the explanation of the fact that the point for PbTe lies off the line is not due merely to erroneous experimental values of the effective masses and/or energy gaps.

It should be mentioned at this point that consideration of the band structures reported by Herman *et al.*[11] for PbS, PbSe, and PbTe show a smooth progression in band structure near L from PbS to PbSe to PbTe. In this respect, the band structures of these lead compounds are similar to those of many III-V and II-VI compounds[22] in that there are no unusual band crossings of the type noted[22] at Γ in the progression from silicon to germanium to grey tin. This point lends support to the view that the lack of a monotonic decrease of the energy gap of the PbX semiconductors with atomic number of X is fundamental, rather than being an effect related to band crossing or other unusual phenomena. It may also be noted that, experimentally, the value of the energy gap of PbTe is larger than the energy gap of PbSe at all temperatures from 4 to 373 °K. This observation indicates that there is no unusual temperature dependence of either the electron-phonon or lattice-expansion contributions to the energy gap to account for the observed values of band gaps.

The most likely explanation of the f-sum rule results is that PbTe does not follow the same f-sum rule as do PbS and PbSe because the value of the matrix element M for PbTe is different, for fundamental reasons, from its value for PbS and PbSe. On comparison with the results of the f-sum-rule plots for those sequences (i.e., InX, GaX, and CdX) exhibiting a regular series of energy-gap values, and also having the same value of M, this irregular value of M for PbTe is indeed unusual. [The observed result for the six-band f-sum-rule plot for PbTe would also be the case if the matrix elements for the various terms in the sum in Eq. (1) were not all the same for PbTe. However, the fact that PbS and PbSe *do* satisfy Eq. (3) shows that the use of a single matrix element N is a good approximation in their case.] In any event, the results obtained suggest the existence of a qualitative difference between the band-edge states at the L point for PbTe and the equivalent states in PbS and PbSe.

It has been suggested by Pratt and Ferreira[23]

TABLE VI. Values of matrix elements calculated from slopes of f-sum-rule plots for PbS, PbSe, and PbTe.

Band p	Total bands	Mass	Matrix element in units of $10^{-14}g^{1/2}(\text{eV})^{1/2}$
		PbS and PbSe	
L_6^-	2	Electrons	$\lvert M_t \rvert = 4.08$
L_6^+	2	Holes	$\lvert M_t \rvert = 4.32$
L_6^-	2	Electrons	$\lvert M_l \rvert = 3.26$
L_6^+	2	Holes	$\lvert M_l \rvert = 3.32$
L_6^-	6	Electrons	$\lvert N_t \rvert = 4.05$
L_6^+	6	Holes	$\lvert N_t \rvert = 4.23$
L_6^-	6	Electrons	$\lvert N_l \rvert = 3.26$
L_6^+	6	Holes	$\lvert N_l \rvert = 3.23$
		PbTe	
L_6^-	2	Electrons	$\lvert M_t' \rvert = 5.92$
L_6^+	2	Holes	$\lvert M_t' \rvert = 6.19$
L_6^-	2	Electrons	$\lvert M_l' \rvert = 1.66$
L_6^+	2	Holes	$\lvert M_l' \rvert = 1.39$
L_6^-	6	Electrons	$\lvert N_t' \rvert = 5.94$
L_6^+	6	Holes	$\lvert N_t' \rvert = 6.48$
L_6^-	6	Electrons	$\lvert N_l' \rvert = 1.66$
L_6^+	6	Holes	$\lvert N_l' \rvert = 1.45$

that the energy-gap variation in the PbS group is related to an anomaly in the outer s-level energies of the sulfur, selenium, and tellurium atoms. Figure 10 shows a plot of the calculated[24] outer s-level energies U of the group-VI atoms (including polonium) as a function of atomic number. The values are: for sulfur, $U(3s^2) = -1.5471$ Ry; for selenium, $U(4s^2) = -1.5749$ Ry; for tellurium, $U(5s^2) = 1.4162$ Ry; and for polonium, $U(6s^2) = -6.227$ Ry. It may be seen that the points for sulfur, selenium, and polonium fall on a good straight line. The point for tellurium, however, definitely does not lie on this line, and the anomaly in this series of electron energies is clearly seen to lie with the tellurium atom.

The unusual behavior of the data for PbTe in the f-sum-rule plots thus correlates with the irregular behavior of the $5s$ electron energy of the tellurium atom. This correlation supports the view that the anomalous energy-gap value and the irregular value of the matrix element M for PbTe are due to a qualitative difference between the band-edge states in PbTe and those in PbS and PbSe. As calculated by Herman *et al.*,[25] the IV-VI semiconductor energy band, at the L point, whose atomic character is that of a group-VI outer-electron s level, is the L_6^- conduction band. For the case under discussion, the relevant group-VI atom is tellurium. It is therefore concluded that the PbTe L_6^- band-edge states differ from the equivalent states in PbS and PbSe because of the irregular $5s$ level energy of the tellurium atom.

This difference in the L_6^- band-edge states of PbTe would cause the matrix element $M = \langle L_6^- | \pi_j | L_6^+ \rangle$, where $j = l$ or t, to have a value for PbTe different from its value for PbS and PbSe. This is the reason that PbTe does not follow the same f-sum rule as do PbS and PbSe.

It would be of interest to calculate (see note added in proof) values of the matrix elements M_j (defined below) where $j = l$ or t, using appropriate wave functions $\langle L_6^- |$ and $| L_6^+ \rangle$, and to compare the calculated results with the values determined, as described below, from experimental data on effective masses and energy gaps. This comparison would be useful in elucidating the nature of the L_6^- conduction-band-edge states in PbTe and, especially, how these states may differ from the equivalent states in PbS and PbSe.

An interesting experimental possibility is the preparation and study of PbPo. A knowledge of whether this IV-VI compound is a semiconductor would be very useful. If it is, a determination of the energy gap (by optical means to avoid the influence of carriers due to defects produced by radiation from the polonium) for comparison with the energy gaps of the other members of the PbX sequence would be of great interest.

The slopes of the straight lines in Figs. 1–6 yield, using Eq. (2) or (3), values for PbS and PbSe of the matrix elements $\langle n, L | \pi_j | p, L \rangle \equiv M_j$ or N_j ($j = l$ or t) for the two-band and six-band models, respectively. The values of $|M_j|$ and $|N_j|$ [in units of $g^{1/2}$ (eV)$^{1/2}$] so determined are shown in Table VI. It may be noted that, within a few percent, $|N_j| = |M_j|$, where $j = l$ or t, for either electrons or holes; additional bands in the f sum do not appreciably alter the slope of the line defined by the points for PbS and PbSe and the origin. In addition, the value of $|M_j|$ or $|N_j|$ ($j = l$ or t) for one choice (L_6^- or L_6^+) of band p is the same within a few percent of the value for the other choice of band p. This is as expected, since it is reasonable that $|\langle L_6^- | \pi_j | L_6^+ \rangle|^2 = |\langle L_6^+ | \pi_j | L_6^+ \rangle|^2$. It may also be noted that $|M_t|$ is about 25% larger than $|M_l|$ for either electrons or holes; the same is true of $|N_t|$ and $|N_l|$. Similarly, the slope of a straight line through the origin and the PbTe point in Figs. 1–6 will provide the value of the analogous matrix elements $|M_j'|$ and $|N_j'|$ for PbTe. These values, calculated using the PbTe point showing the data of Cuff *et al.*,[16] are also given in Table VI. Here also the agreement between matrix elements for the two choices of band p is good.

V. SUMMARY AND CONCLUSIONS

The f-sum rule has been examined at the conduction- and valence-band edges of PbS, PbSe, and PbTe, using experimental values of effective masses and energy gaps. For both two-band and six-band models, it was found that PbTe does *not* follow the same f-sum rule as do PbS and PbSe. On the other hand, for the III-V and II-VI semiconductor sequences InX, GaX, and CdX (hexagonal), the members of each sequence *do* follow the same f-sum rule. These results indicate that the well-known anomaly in the energy-gap values for PbS, PbSe, and PbTe is due to an irregularly large value of the energy gap of PbTe. It appears likely that the anomalous energy-gap value for PbTe reflects, through the L_6^- conduction-band edge, the irregular value of the $5s$ electron energy level of the tellurium atom. It is proposed that the L_6^- conduction-band edge states in PbTe differ from the equivalent states in PbS and PbSe, resulting in PbTe having a different f-sum matrix element from PbS and PbSe. This is the reason that PbTe does not follow the same f-sum rule as do PbS and PbSe. Matrix-element values have been calculated from the slopes of the linear f-sum plots of the experimental data.

Note added in proof. It has come to the author's attention that matrix-element calculations of the type suggested in Sec. IV have been reported by S. Rabii [Phys. Rev. 167, 801 (1968)].

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[*] Visiting Research Associate, 1969–1970. Present address: RCA Laboratories, Princeton, N. J. 08540.

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