INTERBAND TRANSITIONS IN GROUPS 4, 3-5, AND 2-6 SEMICONDUCTORS*

H. Ehrenreich and H. R. Philipp
General Electric Research Laboratory, Schenectady, New York

and

J. C. Phillips
Institute for the Study of Metals, University of Chicago, Chicago, Illinois
(Received December 18, 1961)

Direct interband transitions are believed to be responsible for the peaks observed[1-5] in the reflectivity of a number of semiconductors in the range between 1 and 12 ev. Identification of these transitions should provide insight into the band structure of these crystals over a much wider range of energies than has been possible heretofore. In this Letter new experimental information concerning the reflectance of Ge, InSb, InAs, GaAs, and GaP is presented together with a number of theoretical considerations which permit identification of much of the observed structure. These data are shown in Fig. 1 and the proposed assignments for the observed peaks are summarized in Table I. This table also includes information concerning C, Si, and ZnSe obtained from data[6,2,5] published elsewhere. The data shown in Fig. 1 were obtained on etched samples at 300°K employing a vacuum monochromator. Fine structure between 4 and 7 ev was examined in greater detail by balancing out 90% of the detector photocurrent so that the remaining 10% containing the structure could be considerably amplified. Weak structure observed in the original data, and referred to in Table I, is clearly identifiable in expanded scale drawings.

The $L_3' \rightarrow L_1$ transitions shown in Table I have been previously identified[7,8,4] using the characteristic spin-orbit splitting of L_3' as a guide. The $L_3' \rightarrow L_3$ transitions should also exhibit similar splitting. Phillips and Liu[9] have calculated the spin-orbit splitting of L_3 and L_3' in Ge and several zinc blende-type semiconductors. They find the spin-orbit splitting of L_3 to be small compared to L_3'. Thus one expects this transition to be associated with only a twofold splitting which should be the same as that characterizing $L_3' \rightarrow L_1$. This feature is indeed observed although the splitting in InAs is somewhat larger than expected. Further, Phillips[10] has argued that since the $L_3' \rightarrow L_3$ and $\Gamma_{25'} \rightarrow \Gamma_{15}$ gaps in germanium have been shown[11] to be relatively insensitive to the choice of the core potential, the observed peaks should be expected to agree with the results of band calculations. For Ge and Si the calculated $L_3' \rightarrow L_3$ gaps are[11] 6.0 and[12] 5.4 ev, respectively, in almost precise correspondence to the experimentally observed structure here ascribed to $L_3' \rightarrow L_3$.

A plot of the $L_3' \rightarrow L_3$ gap for the horizontal sequence Ge, GaAs, ZnSe vs λ^2, where λ is Herman's parameter[13] characterizing the strength of the perturbing antisymmetric potential modifying the Ge potential, yields the expected straight line. As Callaway has shown,[14] the L_3'

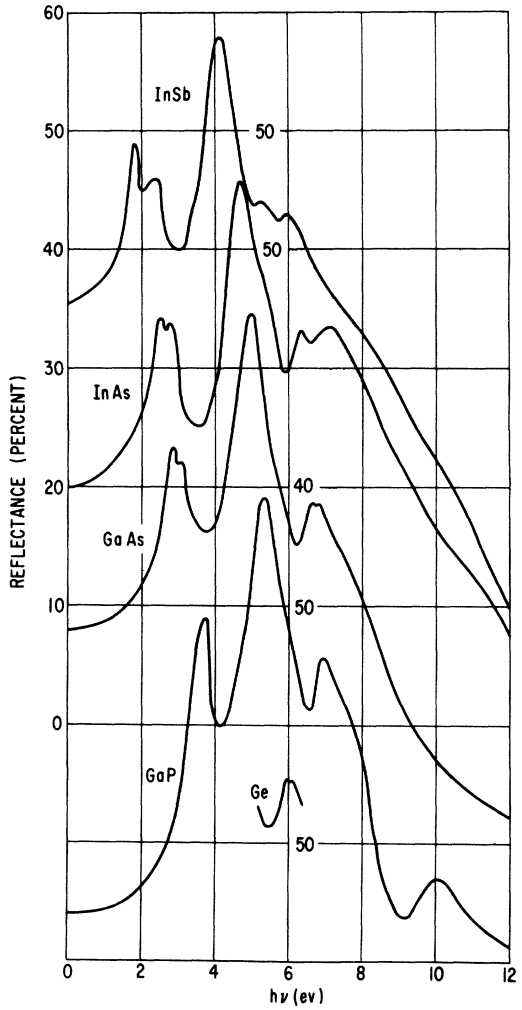

FIG. 1. Reflectance of InSb, InAs, GaAs, GaP, and Ge vs photon energy.

Table I. Energy gaps deduced from reflectance data. Double entries correspond to peaks split by spin-orbit interaction.

	$L_{3'} \rightarrow L_1$	$L_{3'} \rightarrow L_3$	$\Gamma_{25'} \rightarrow \Gamma_{15}$	$X_4 \rightarrow X_1$ $X_5 \rightarrow X_1$	$X_5 \rightarrow X_3(?)$
C		9	7.0	12.7	...
Si	3.7	5.5	3.5	4.5	...
Ge	2.1 2.3	5.9 6.1	3.1	4.5	...
GaP			3.7(?)	5.3	
GaAs	2.9 3.1	6.6 6.9		5.0	5.9
InAs	2.5 2.8	6.4 7.0	5.2	4.7	
InSb	1.8 2.4	5.3 6.0	3.4	4.1	
ZnSe	4.9 5.3	9.1 9.6		6.7	8.5

and L_3 levels repel each other under the influence of this perturbation. From the observed slope the calculated matrix element which determines this repulsion corresponds to 1.5 ev in comparison to the value 0.9 ev estimated by Callaway within an assigned accuracy of about 50%.

Phillips[10] suggested that the same argument applies to the $\Gamma_{25'} \rightarrow \Gamma_{15}$ gap which is also insensitive to the core potential. The 3.5-ev peak in Si and the previously unidentified shoulder at 3.1 ev in Ge, corresponding to calculated values of[12] 2.6 and[11] 3.0 ev, respectively, should therefore be assigned to this transition rather than $L_{3'} \rightarrow L_3$ as previously suggested. That these peaks correspond to the same transition follows from the data on Ge-Si alloys.[3] Further corroborating evidence comes from the observed cyclotron resonance constants. The ratio[15,16] H_1^{Ge}/H_1^{Si} is equal to the inverse ratio 3.5/3.1 of the observed gaps in Si and Ge. This agreement is expected if the momentum matrix elements connecting the $\Gamma_{25'}$ and Γ_{15} levels are about the same in the two materials.[10] Furthermore the values of $H_1 = (\hbar^2/2m) \times E_p(\Gamma)/[E(\Gamma_{25'}) - E(\Gamma_{15})]$ themselves are consistent with these gaps for a reasonable value of $E_p(\Gamma)$, proportional to the square of the momentum matrix element connecting $\Gamma_{25'}$ and Γ_{15}, of 15 ev.

In the case of InAs, Matossi and Stern[16] have deduced a value $H_1 = -3.0(\hbar^2/2m)$ from a theoretical fit of the free-hole absorption. Since the matrix elements determining E_p appear to vary very little in related materials,[10,17] the $\Gamma_{25'} \rightarrow \Gamma_{15}$ gap can be calculated to be 5.0 ev from this value of H, using the Ge value of $E_p(\Gamma) = 15$ ev. The observed shoulder near 5.2 ev in the reflectance of InAs is thus assigned to the $\Gamma_{25'} \rightarrow \Gamma_{15}$ transition. The weak structure near 3.4 ev in InSb also probably corresponds to this transition. The heavy-hole mass is known to be most strongly influenced by the $\Gamma_{25'} \rightarrow \Gamma_{15}$ and $\Gamma_{25'} \rightarrow \Gamma_{12'}$ gaps.[18] This gap in InSb is quite consistent with a heavy-hole mass of [19] 0.4 ± 0.1 if the $\Gamma_{25'} \rightarrow \Gamma_{12'}$ gap is about 10 ev as it is in Ge.

The antisymmetric potential that is introduced in passing from Ge to GaAs produces a repulsion between the $\Gamma_{25'}$ and Γ_{15} levels.[14] This causes the gap to increase by about 1.6 ev if the matrix element can be assumed to be the same as that producing the repulsion between the $L_{3'}$ and L_3 levels, which also have p-like character. The expected structure near 4.6 ev in GaAs would, however, be masked by stronger transitions near X in this energy range. The 3.7-ev peak in GaP has been attributed[20] to the transitions identified in this Letter with $\Gamma_{25'} \rightarrow \Gamma_{15}$.

The interpretation of the strongest reflectivity peak at 4.5 ev in Ge in terms of $X_4 \rightarrow X_1$ transitions has been criticized[21] on the grounds that

the behavior of the dielectric constants in this region does not correspond to that expected for a band edge according to Korovin's theory,[22] but is rather that of an oscillator and thus identifiable with a maximum of the joint density of states somewhere in the Brillouin zone. However, it may be shown that the behavior of the dielectric constants corresponding to a band edge may indeed closely resemble that of an oscillator when deviations from parabolicity, neglected by Korovin, became important near the edge in question. In view of the fact that the $X_4 \rightarrow X_1$ gap is insensitive to the core potential,[11] the agreement between calculated values for this gap (13.6,[23] 4.7,[12] and[11] 4.6 ev in C, Si, and Ge, respectively) and observed values of the large reflectance peak (12.7,[6] 4.5,[2] and[1] 4.5 ev) leads to an unambiguous assignment of the peaks to a transition at or quite near X. In addition, plots of the $X_4 \rightarrow X_1$ or $X_5 \rightarrow X_1$ gap vs λ^2 for the horizontal sequences, Ge, GaAs, ZnSe, and Sn[20] (3.65 ev), InSb and CdTe (5.4 ev), yield straight lines showing that the same transition is involved in each case.

In the 3-5 and 2-6 compounds the twofold degeneracy at X_1 is lifted. The gap associated with the resulting X_1 and X_3 levels is expected to increase as λ for a horizontal sequence. The observed peaks at 5.9 ($\lambda = 1$) and 8.5 ev ($\lambda = 2$) in GaAs and ZnSe, together with the 4.5-ev peak in Ge ($\lambda = 0$), appear to satisfy this relationship and hence are assigned tentatively to this transition. Despite the strong evidence to the contrary, the possibility that the 5.2-ev peak in InAs corresponds to $X_5 \rightarrow X_3$ rather than the $\Gamma_{25'} \rightarrow \Gamma_{15}$ transition cannot be completely discarded at the present time. Further the 8.5-ev peak in ZnSe attributed here to $X_5 \rightarrow X_3$ transitions may very well be part of the $L_{3'} \rightarrow L_3$ structure if the L_3 splitting is comparable to that of $L_{3'}$ in this material.

In addition to the peaks already discussed there is additional structure in the curves shown in Fig. 1 which is not interpretable without band structure calculations for these materials. This structure may be due to additional bands at the points X, L, and Γ or at new points in the Brillouin zone such as W. In particular, the $\Gamma_{25'} \rightarrow \Gamma_{12'}$ transition might be one of those observed because this gap and its corresponding matrix element influences importantly the value of the heavy-hole mass.

---

*One of the authors (JCP) acknowledges partial support from the Office of Naval Research.

[1]H. R. Philipp and E. A. Taft, Phys. Rev. 113, 1002 (1959).

[2]H. R. Philipp and E. A. Taft, Phys. Rev. 120, 37 (1960).

[3]J. Tauc and A. Abraham, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences Publishing House, Prague, 1961), p. 375.

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

[5]M. Aven, D. T. F. Marple, and B. Segall, Suppl. J. Appl. Phys. 32, 2261 (1961).

[6]E. A. Taft and H. R. Philipp, Bull. Am. Phys. Soc. (to be published).

[7]J. C. Phillips, J. Phys. Chem. Solids 12, 208 (1960).

[8]J. Tauc and E. Antončík, Phys. Rev. Letters 5, 253 (1960).

[9]J. C. Phillips and L. Liu (to be published).

[10]J. C. Phillips, Phys. Rev. (to be published).

[11]F. Herman and S. Skillman, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences Publishing House, Prague, 1961), p. 20.

[12]L. Kleinman and J. C. Phillips, Phys. Rev. 118, 1153 (1960).

[13]F. Herman, J. Electronics 1, 103 (1955).

[14]J. Callaway, J. Electronics 2, 330 (1957).

[15]G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. 98, 368 (1955).

[16]F. Matossi and F. Stern, Phys. Rev. 111, 472 (1958).

[17]H. Ehrenreich, Suppl. J. Appl. Phys. 32, 2155 (1961).

[18]E. O. Kane, J. Phys. Chem. Solids 1, 249 (1957).

[19]F. Stern, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences Publishing House, Prague, 1961), p. 363.

[20]M. Cardona (to be published).

[21]M. Cardona and H. S. Sommers, Jr., Phys. Rev. 122, 1382 (1961).

[22]L. I. Korovin, Fizika Tverdoga Tela U.S.S.R. 1, 1311 (1959)[translation: Soviet Phys. —Solid State 1, 1202 (1960)].

[23]L. Kleinman and J. C. Phillips, Phys. Rev. 117, 460 (1960).