

tions. One should here mention that the original calculation of Galt<sup>6</sup> which is supposed to be made on the basis of the same model used by Clogston<sup>7</sup> yields an equation of the desired type [Eq. (4)]. However, it is believed that this analysis is not correct because of Galt's handling of the relaxation term. Clogston uses a relaxation term that describes relaxation toward the instantaneous magnetic field while Galt's term relaxes toward a different field.<sup>23</sup> This is analogous to the problem discussed in Sec. II on the application of the Bloch-Bloembergen equation.

Although we cannot justify it theoretically the empirical equation [Eq. (9)] does provide an excellent fit to the data, and it is useful, in closing, to review the main features of this agreement. *Firstly*, we have assumed well-known relaxation processes which are believed to be appropriate for the rare-earth ions in the garnets. *Secondly*, using these processes the temperature dependence of the linewidth is accounted for. *Thirdly*, in fitting Eq. (9) to the data two parameters are evaluated, the exchange frequency ( $\omega_{ex}$ ) and the coefficient

<sup>23</sup> This was pointed out to the author by A. J. Heeger. In addition, it has previously been noted that the energy loss obtained from this theory is not positive definite (Ref. 7).

of the rare-earth relaxation term ( $K_1$  and  $K_2$ ). In the cases where comparison with independent measurements is possible good agreement is found. *Fourthly*, the frequency dependence of the temperature of the linewidth peak and the linewidth at the peak obtained from Eqs. (12) and (13) is in excellent agreement with experiment. *Finally*, there are no adjustable parameters remaining in the analysis. Of course there *still* remains the problem of justifying Eq. (9) on theoretical grounds but such an excellent fit to experiment makes it very plausible that a relation of this sort should be the correct one.

Lastly, it should be noted that even if this relation should prove to be correct so that one would be able to account for the linewidth behavior there would still remain the intriguing problem of why some ions relax by the direct process and others by the Orbach process.

#### ACKNOWLEDGMENTS

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## Reflectivity of HgSe and HgTe from 4 to 12 eV at 12 and 300°K

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The reflectivity of etched samples of HgSe and HgTe has been measured from 4–12 eV (3000–1050 Å) at room and He temperatures. Several peaks found in the reflectivity spectrum have been assigned to interband transitions at the  $L$  and  $X$  points in the Brillouin zone. Doublets, which are due to the effect of spin-orbit interaction, are resolved when the samples are cooled to He temperature. The values for  $L_3$  splitting (valence band) for both HgSe and HgTe are in agreement with other measurements of these materials in the visible region where a doublet due to  $L_{2V}$ – $L_{1C}$  transitions is found. Other transitions are also discussed.

### I. INTRODUCTION

IN recent years, the measurement of the optical reflectivity of semiconductors in the visible and ultraviolet has given much information concerning interband transitions and the over-all band structure of both diamond and zincblende structure materials.<sup>1</sup> The simi-

larities in the reflectivity spectra of semiconductors, and the known general appearance of the band structure for the diamond and zincblende materials have been helpful in interpreting the data. In addition, detailed band structure calculations on Ge and Si have supported the interpretations.<sup>2</sup> While the cumulative evidence makes the identifications very plausible, it should be noted that no experiments reported have demonstrated the symmetry of the states involved in the transitions.

In this paper, we report on reflectivity measurements

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<sup>1</sup> H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959); **120**, 37 (1960); J. Tauc and A. Abraham, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Science, Prague, 1961); M. Cardona, J. Appl. Phys. Suppl. **32**, 2151 (1961); H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters **8**, 59 (1962); H. R. Philipp and H. Ehrenreich, *ibid.* **8**, 92 (1962); R. E. Morrison, Phys. Rev. **124**, 1314 (1961); M. Cardona and D. L. Greenaway, *ibid.* **125**, 1291 (1962); D. L. Greenaway, Phys. Rev. Letters **9**, 97 (1962); H. R. Philipp and H. Ehrenreich, Phys. Rev. **129**, 1550

(1963); M. Cardona and G. Harbeke, J. Appl. Phys. **34**, 813 (1963); M. Cardona and D. L. Greenaway, Phys. Rev. **131**, 98 (1963); J. C. Phillips, J. Phys. Chem. Solids **12**, 208 (1960).

<sup>2</sup> J. C. Phillips and L. Liu, Phys. Rev. Letters **8**, 94 (1962); J. C. Phillips, Phys. Rev. **125**, 1931 (1962); D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters **9**, 94 (1962).

which were made on HgSe and HgTe between 4 and 12 eV. These materials are II-VI compounds with a zincblende structure. Their reflectivity spectra are similar to those of the III-V compounds.<sup>3</sup> When the samples are cooled to helium temperature, additional fine structure is observed.

The peaks in the reflectivity spectra are interpreted in terms of interband transitions on the basis of an energy band picture similar to that of the III-V compounds. In addition, spin-orbit interaction in these mercury compounds causes a splitting which is observed in transitions not only from the  $L_3$  valence band point, but also from the  $X_5$  point.

## II. PROCEDURE

The reflectivity measurements were made using a modified McPherson model-240 vacuum ultraviolet spectrograph. The samples were mounted in a cryostat in a special sample chamber designed to prevent contamination of the sample surface at helium temperature. The details of this apparatus will be reported in another paper.<sup>4</sup>

For each material, two samples were cut from each of two ingots. The samples were polished and etched in suitable chemical mixtures.<sup>5</sup> Immediately after etching, each sample was mounted in the cryostat and pumping was begun.

The reflectivity was measured for all samples at both 300 and 12°K. The temperature was measured with a thermocouple which was silver cemented to the sample holder in the same manner as the sample.

The reproducibility of the signal from the light source

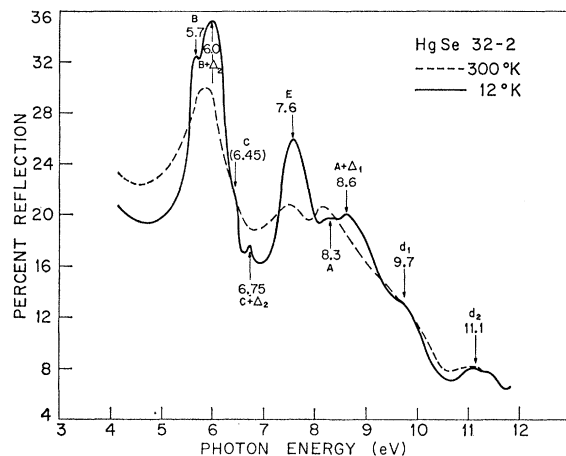


FIG. 1. Reflectivity of HgSe at 300 and 12°K.

<sup>3</sup> See Ref. 1: e.g., Tauc and Abraham; Cardona; Ehrenreich, Philipp and Phillips; Greenaway.

<sup>4</sup> W. J. Scouler, Appl. Opt. (to be published).

<sup>5</sup> HgSe etch;  $\text{HNO}_3:\text{CH}_3\text{COOH}:18\text{N H}_2\text{SO}_4:\text{HCl}-50:10:20:1$ .  $\text{H}_2\text{O}$  rinse. HgTe etch;  $\text{HCl}:\text{HNO}_3:\text{CH}_3\text{OH}-1:6:2$ . Add  $\text{CH}_3\text{OH}$  after acids have mixed to orange-red color. Rinse  $\text{HCl}:\text{CH}_3\text{OH}-1:1$ . Rinse  $\text{H}_2\text{O}$ . See also, E. P. Warekois, M. C. Lavine, A. N. Mariano, and H. C. Gatos, J. Appl. Phys. **33**, 690 (1962).

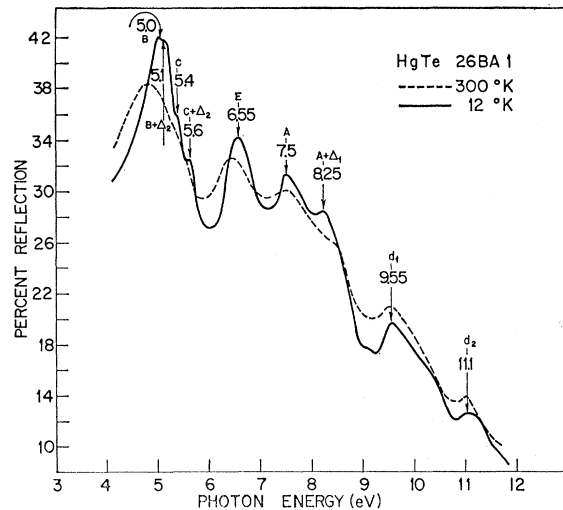


FIG. 2. Reflectivity of HgTe at 300 and 12°K.

and spectrometer was a few parts per thousand over most of the spectrum.<sup>6</sup> In regions of weak fine structure, repeated measurements were made to ensure that the peaks were real. Since the etched sample surfaces were not always mirror-like, scattering could cause an estimated error in the absolute reflectivity of five parts per hundred. However, the reflectivity, neglecting this error due to scattering, is accurate to a few parts per thousand.

## III. RESULTS AND DISCUSSION

Figures 1 and 2 show the reflectivity versus photon energy for typical samples of HgSe and HgTe, respectively, at 300 and 12°K. Considerable fine structure is resolved when the samples are cooled. This fine structure was observed in all samples, and is very similar to that observed by Marple<sup>7</sup> in the reflectivity of CdTe at 24°K. Cardona and Greenaway<sup>8</sup> have also observed some fine structure around 5 eV in HgTe at 77°K.

Table I indicates the labeling and assignments which have been made concerning the peaks. Peaks which are assigned to the same transitions in the two materials are labeled with the same letters. The subscripts  $V$  and  $C$  refer to valence band and conduction band, respectively. The  $\Delta$ 's refer to spin-orbit splitting which will be discussed subsequently. Since more structure is observed at 12°K, the remainder of the discussion will refer to the low-temperature reflectivity curves.

As has already been mentioned, the shape of the reflectivity curves for HgSe and HgTe is similar to that for the III-V compounds.<sup>3</sup> We have therefore used the systematic trends established for the III-V's to identify our reflectivity structure in terms of transitions at vari-

<sup>6</sup> W. J. Scouler and E. D. Mills (to be published).

<sup>7</sup> D. F. Marple (private communication). The authors wish to thank Dr. Marple for making available his results prior to publication.

<sup>8</sup> M. Cardona and D. L. Greenaway, Phys. Rev. **131**, 98 (1963).

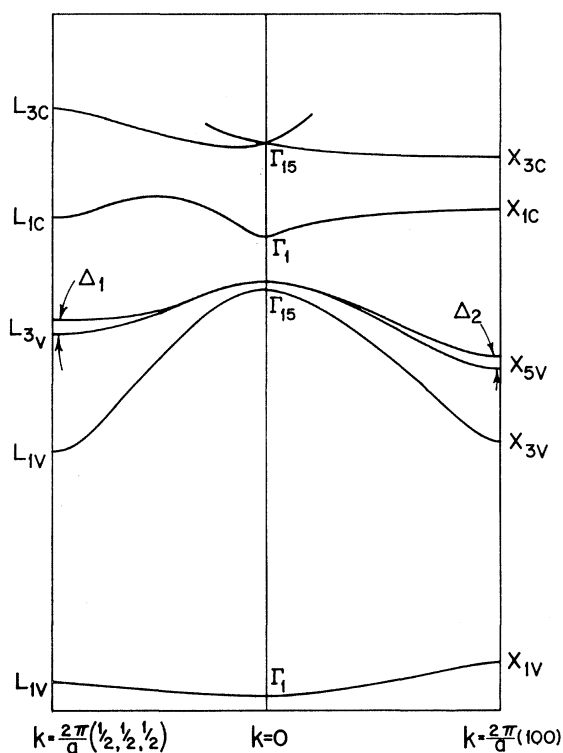
TABLE I. Identification of reflectivity peaks for HgSe and HgTe at 12°K. *V* and *C* subscripts refer to valence and conduction band, respectively.  $\Delta_1$  and  $\Delta_2$  are spin-orbit splitting values at the  $L_{3V}$  point and  $X_{5V}$  point, respectively.  $X_{3C}-X_{1C}$  gap in conduction band.

Identification	Transition label	$L_{3V}-L_{3C}$ $A, A+\Delta_1$	$X_{5V}-X_{1C}$ $B, B+\Delta_2$	$X_{5V}-X_{3C}$ $C, C+\Delta_2$	<i>d</i> bands $d_1, d_2$	...	$L_{3V}$ S-O $\Delta_1$	Splittings	
								$X_{5V}$ S-O $\Delta_2$	$X_{3C}-X_{1C}$ <i>C-B</i>
Peak positions in eV	HgSe	8.3, 8.6	5.7, 6.0	6.45, 6.75	9.7, 11.1	7.6	0.3	0.3	0.75
	HgTe	7.5, 8.25	5.0, 5.1	5.4, 5.6	9.55, 11.1	6.55	0.75	0.1-0.2	0.4-0.5

ous points in the Brillouin zone.<sup>9</sup> These identifications will now be discussed.

### 1. Transitions at *L*

Spin-orbit splittings have been of great assistance in identifying transitions between valence and conduction bands in semiconductors.<sup>1,2</sup> The peaks *A* and  $A+\Delta_1$  have been assigned to transitions between the  $L_3$  point in the valence band,  $L_{3V}$ , and the  $L_3$  point in the conduction band,  $L_{3C}$ , where  $\Delta_1$  is the splitting due to spin-orbit interaction at the  $L_{3V}$  point (Fig. 3).



ZINC BLENDE ENERGY BAND STRUCTURE

FIG. 3. Zincblende energy band diagram.

<sup>9</sup> A Kramers-Kronig analysis to determine the optical constants, *n* and *k*, is often performed on reflectivity data but since the plot for *k* ( $=\alpha\lambda/4\pi$ ) versus photon energy follows the reflectivity curve shape closely, we equate peaks in reflectivity with peaks in absorption.

<sup>10</sup> M. Cardona, J. Appl. Phys. Suppl. 32, 2151 (1961).

This assignment is based on the good agreement of our  $\Delta_1$  values for both HgSe and HgTe with the splitting observed in  $L_{3V}-L_{1C}$  transitions around 2 eV.<sup>10</sup>

However, in the case of HgTe, Cardona and Greenaway<sup>8</sup> have with some reservations, attributed their room temperature peaks at 6.55 and 7.8 eV to spin-orbit split  $L_{3V}-L_{3C}$  transitions. This would give a  $\Delta_1$  value of 1.25 eV, which they note is much larger than the  $\Delta_1$  value of 0.7 eV derived from  $L_{3V}-L_{1C}$  transitions.

The helium-temperature data of this work show additional structure compared to the room-temperature data and define peaks for HgTe at 7.5 eV (*A*) and 8.25 eV ( $A+\Delta_1$ ). We believe that these peaks are due to spin-orbit split  $L_{3V}-L_{3C}$  transitions giving the more reasonable  $\Delta_1$  value of 0.75 eV which agrees with the data in the visible. A possible interpretation for the peak at 6.55 eV (*E*) will be discussed subsequently.

Comparison of peak locations for  $L_{3V}-L_{1C}$  and  $L_{3V}-L_{3C}$  transitions in the visible and ultraviolet, respectively, gives for both HgSe and HgTe, an  $L_{1C}-L_{3C}$  gap of 5.5 eV.

Table II lists the available  $\Delta_1$  values for II-VI selenides and tellurides. It is reasonable to expect that both constituents of the compounds contribute to the spin-orbit interaction as has been suggested by Braunstein and Kane.<sup>11</sup> Since the table indicates that the  $\Delta_1$  value changes little as the cation is varied, it appears that the Group VI element is much more influential in the II-VI's than the Group V element in the III-V's. This is expected since the II-VI's should be more ionic

TABLE II. Values of spin-orbit splitting at the  $L_{3V}$  point for some II-VI compounds.

	$\Delta_1(L_{3V})$ in eV			Free ion
	Zn	Cd	Hg	
Selenides	0.35 <sup>a</sup>	0.28 <sup>c,d</sup>	0.30	Se <sup>-</sup> 0.29 <sup>f</sup>
Tellurides	0.57 <sup>b</sup>	0.55 <sup>b,e</sup>	0.75	Te <sup>-</sup> 0.65 <sup>f</sup>

<sup>a</sup> M. Aven, D. F. Marple, and B. Segall, J. Appl. Phys. Suppl. 32, 2261 (1961).

<sup>b</sup> M. Cardona and D. L. Greenaway (see Ref. 8).

<sup>c</sup> M. Cardona, Phys. Rev. 129, 1068 (1963).

<sup>d</sup> Wurtzite structure.

<sup>e</sup> D. F. Marple (private communication).

<sup>f</sup> G. A. Saum and E. B. Hensley (see Ref. 14).

<sup>11</sup> R. Braunstein and E. O. Kane, J. Phys. Chem. Solids 23, 1423 (1962).

in character<sup>12</sup>; that is, the electrons are shared less equally by the constituents in the II-VI's. This in turn implies that the anion contributes more to the total spin-orbit interaction.

Numerical estimates of spin-orbit values in the solid are based on atomic spin-orbit values of the constituents.<sup>11,13</sup> The one electron spin-orbit value of the atom, in turn, depends on the type of spin-orbit coupling ( $\mathbf{L}\cdot\mathbf{S}$  or  $\mathbf{j}\cdot\mathbf{j}$ ). In general,  $\mathbf{L}\cdot\mathbf{S}$  coupling does not hold well for heavy atoms as is the case here. In addition, going from the spin-orbit values of the atom to spin-orbit values of the solid involves the use of normalization factors, and also the use of ionicity weighting factors which determine the amount that each of the constituent atoms contributes to the over-all spin-orbit interaction. All these parameters are flexible enough so that the conclusions which are drawn from such a numerical analysis are only suggestive. The experimental values of  $\Delta_1$  observed in the II-VI's however, are in reasonable agreement with calculations based on such an analysis.<sup>13</sup>

It is interesting to note that the free-ion values of Saum and Hensley<sup>14</sup> are close to the experimental  $\Delta_1$  values.  $\text{Hg}^+\text{Se}^-$  or  $\text{Hg}^+\text{Te}^-$  would be very ionic compounds (12–88%) but not unreasonable ones.

## 2. Transitions at $X$

In germanium the energy bands at  $X$  are all doubly degenerate, as required by symmetry. In the zincblende structure there are two different sublattices and splitting is allowed. The conduction band at  $X$  will be split into two levels  $X_{1C}$  and  $X_{3C}$  even in the absence of spin-orbit interaction. The valence band at  $X_{5V}$  will only be split by spin-orbit interaction which should be proportional to a weighted difference of the spin-orbit splitting of the two sublattice ions.<sup>13</sup>

When HgSe and HgTe were cooled to 12°K, the reflectivity peak normally identified with transitions at  $X$  did show fine structure. These peaks are labeled  $B$ ,  $B+\Delta_2$  and  $C$ ,  $C+\Delta_2$ . The doublet at  $B$  corresponds to spin-orbit split  $X_{5V}-X_{1C}$  transitions and the doublet at  $C$  to spin-orbit split  $X_{5V}-X_{3C}$  transitions. In HgTe,  $\Delta_2$  at  $B$  and at  $C$  are not identical because it is difficult to locate exactly the peak positions on the steep curve. The difference between  $B$  and  $C$  gives an  $X_{1C}-X_{3C}$  gap of 0.75 eV in HgSe and 0.4–0.5 eV in HgTe. The spin-orbit splitting values are  $\Delta_2=0.3$  eV and 0.1–0.2 eV, respectively.

One notes that the observed  $\Delta_1$  and  $\Delta_2$  in HgSe are equal and that in HgTe they are quite different. Since  $\Delta_1$  is proportional to the sum of the weighted atomic spin-orbit contributions and  $\Delta_2$  is proportional to the difference of the atomic contributions,  $\Delta_1=\Delta_2$  implies

<sup>12</sup> E. Burstein and P. Egli, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. VII, p. 155.

<sup>13</sup> E. L. Krieger and B. Segall, *Bull. Am. Phys. Soc.* **8**, 51 (1963). The authors wish to thank Dr. Segall for additional information concerning calculations.

<sup>14</sup> G. A. Saum and E. B. Hensley, *Phys. Rev.* **113**, 1019 (1959).

that in HgSe, the anion must be weighted much more heavily than in HgTe. Taking this into account, the calculations for  $\Delta_2$  again give reasonable agreement with experimental values.<sup>13</sup> As was the case in the calculation of  $\Delta_1$ , the parameters involved in calculating  $\Delta_2$  are sufficiently flexible so that the numbers derived must only be considered suggestive evidence for the interpretations given.

## 3. Other Transitions

It has been pointed out that observed peaks around 10 eV in HgTe are probably due to transitions between  $d$  electron levels and the conduction band.<sup>8</sup> In our case, we observe peaks at 9.7 and 11.1 eV in HgSe and 9.55 and 11.1 eV in HgTe.

There is additional evidence supporting these  $d$ -band assignments. Philipp and Ehrenreich<sup>15</sup> show that  $d$ -band excitations in solids obtained by optical and electron-loss measurements, can be correlated with atomic excitations between filled  $d$  shells and  $p$  levels in the metal ion. Their results indicate that the  $d$ -band excitation energies in solids are considerably less than the atomic  $d$  to  $p$  transitions. For example, in zinc, the atomic  $d$  to  $p$  transitions are around 18 eV while the observed  $d$ -band transition in ZnTe is around 13 eV. If one assumes a similar situation in mercury, one finds that since atomic  $d$  to  $p$  transitions ( $5d^{10}\rightarrow 5d^96p$ ) occur around 15–16 eV,<sup>16</sup> one might expect to find  $d$ -band excitations in HgTe around 10 eV.

There is evidence that there are overlapping bands in HgSe and HgTe producing semimetal behavior.<sup>17</sup> Considerable mixing of states is possible since the valence band may be strongly perturbed by nearby lower  $d$  levels. This mixing could be responsible for the overlap and also result in the unexplained prominent peak at  $E$  which would correspond to transitions from the overlapping band. Another possibility, is that the peak at  $E$  may be due to transitions between other critical points<sup>2</sup> in the Brillouin zone.

In summary, we have found that the reflectivity spectra of HgSe and HgTe can be adequately explained using the energy-band picture of the III-V zincblende compounds as our guide. Obviously, a detailed band calculation would make possible a firmer identification.

## ACKNOWLEDGMENTS

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<sup>15</sup> H. R. Philipp and H. Ehrenreich, *Phys. Rev.* **129**, 1550 (1963).

<sup>16</sup> C. E. Moore, *Nat. Bur. Std. (U. S.) Circ.* **467** (1949), Vol. III, p. 191.

<sup>17</sup> T. C. Harman and A. J. Strauss, *J. Appl. Phys. Suppl.* **32**, 2265 (1961); A. J. Strauss, T. C. Harman, J. G. Mavroides, D. H. Dickey, and M. S. Dresselhaus, in *Proceedings of International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 703.