

# FUNDAMENTAL REFLECTION SPECTRA OF $Zn_x Cd_{1-x}Te$ CRYSTALS IN THE 2.5 TO 4.5 eV RANGE AT ROOM AND LIQUID NITROGEN TEMPERATURES

BY A. KISIEL

Institute of Physics, Jagellonian University, Cracow\*

(Received July 20, 1970)

The reflectivity of light for ZnTe, CdTe and their solid solutions  $Zn_x Cd_{1-x}Te$  ( $x = 0.25, 0.50, \text{ and } 0.75$ ) within the light energy range of 2.5 to 4.5 eV at room and liquid nitrogen temperatures have been measured.

The energies of the  $E_1$  and  $E_1 + \Delta_1$  peaks have been determined. They are for CdTe 3.28 and 3.87 eV at room temperature, and 3.41 and 4.27 eV at liquid nitrogen temperature. For ZnTe the respective values are 3.57 and 4.16 eV, and 3.70 and 4.27 eV. These results are in good agreement with those obtained earlier.

At liquid nitrogen temperature a threshold of energy 3.22 eV, interpreted as an  $e_1$  transition, was found in CdTe. At room temperature there are peaks 3.71 eV ( $e_1 + \Delta_1$ ) and 3.56 eV. It is shown that the temperature coefficients for ZnTe and CdTe are identical within error limits for the  $E_1$  and  $E_1 + \Delta_1$  transitions, but those for  $E_1$ ,  $E_1 + \Delta_1$ , and  $e_1$ ,  $e_1 + \Delta_1$  differ by about 30 per cent.

On the basis of the obtained results a plausible interpretation of the transitions in the band structure is discussed.

## 1. Introduction

It is well known that analysis of the reflection spectrum of light provides important information about the band structure of semiconductors. The relation between optical constants and band structure has been the subject of many publications [1, 2, 3].

The reflection spectra of light have been studied within a broad range of energies for most of the known semiconductors, and the positions of energy peaks in them have been determined with good accuracy by the electro-reflection [4, 5, 6], piezo-reflection [7] and electro-piezo-reflection [8, 9] techniques.

There is still no method, however, which would assign the peaks in the reflection spectrum unambiguously and reliably to transitions between the valence and conductivity bands at different points of the Brillouin zone.

Electro-reflection [4, 5, 6], piezo-reflection (in germanium [7]), electro-piezo-reflection [8, 9], spin-orbit splittings [14] at different points of the Brillouin zone, and temperature coefficients of reflection peaks are all sources of information on band structure. In addition,

\* Address: Instytut Fizyki UJ, Kraków, Reymonta 4, Polska.

more data is also available from the dependence of energy changes of reflection peaks on composition of appropriately chosen solid solutions [10–13].

The reflection spectra of ZnTe and CdTe observed in the 2.5 to 4.5 eV range consist of two distinct peaks, ascertained by Cardona and Greenaway [3] to be  $E_1$  and  $E_1 + \Delta_1$  transitions, and three thresholds  $E_0 + \Delta_0$ ,  $e_1$  and  $e_1 + \Delta_1$  situated on the slopes of the  $E_1$  and  $E_1 + \Delta_1$  peaks.

On the basis of data obtained for Ge by Brust *et al.* [14], Cardona and Greenaway associated the  $E_1$  and  $E_1 + \Delta_1$  peaks observed in CdTe, ZnTe and HgTe with transitions between the valence and conduction bands at the  $\Delta$  point of the Brillouin zone. The thresholds,  $e_1$  and  $e_1 + \Delta_1$ , are assumed to be associated with transitions at the  $L$  point of the Brillouin zone.

The state of research concerning the above transitions has been analyzed by Pollak [15]. Since theoretical calculations performed for CdTe and ZnTe by the OPW [16, 18],  $\mathbf{k} \cdot \mathbf{p}$  [15], KKR [19] and pseudopotential (CB) methods [20] yield one singularity, or perhaps two lying closely together, he concluded that "(1) either the calculations require adjustment or (2) a new interpretation of  $e_1$  and  $e_1 + \Delta_1$  must be found".

The doubts expressed by Pollak form the starting point of the present paper. Because of the lack of reliable identification criteria for the transitions between bands in semiconductors, accumulation of further experimental data concerning the properties of the  $E_1$ ,  $E_1 + \Delta_1$ ,  $e_1$ , and  $e_1 + \Delta_1$  transitions seems to be reasonable.

This paper presents the results of experiments on reflection of light for ZnTe, CdTe and a few their solid solutions in the 2.5 to 4.5 eV range at room and liquid nitrogen temperatures. Also, an attempt to interpret the observed spectra is made.

## 2. Experimental

The reflection measurements were performed on a white light beam with the apparatus described in Ref. [13]. The light source was a hydrogen lamp. Freshly cleaved monocrystals of ZnTe, CdTe, and their solid solutions  $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$  ( $x = 0.25, 0.50, 0.75$ ), prepared at the Institute of Physics of the Polish Academy of Sciences in Warsaw by the method described in Ref. [21], were used. Measurements were performed in the energy range from 2.5 to 4.5 eV at room and liquid nitrogen temperatures. The energy of the  $E_1$  and  $E_1 + \Delta_1$  peaks were determined with an accuracy better than 0.01 eV, while the error of  $e_1$  and  $e_1 + \Delta_1$  was approximately 0.02 eV. The spectra obtained for ZnTe, CdTe and the solid solutions  $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$  are depicted in Fig. 1. Results determined for CdTe and ZnTe are arranged in Table I. The dependence of the position of the  $E_1$ ,  $E_1 + \Delta_1$ ,  $e_1$ ,  $e_1 + \Delta_1$  and  $E_0 + \Delta_0$  peaks on composition for room and liquid nitrogen temperatures is shown in Fig. 2.

## 3. Discussion

In the spectra of light reflected off ZnTe within the 2.5 to 4.5 eV range at room and liquid nitrogen temperatures there are two high, distinct peaks,  $E_1$  and  $E_1 + \Delta_1$ , and three weak but quite discernible thresholds  $E_0 + \Delta_0$ ,  $e_1$  and  $e_1 + \Delta_1$ . The energies of all these peaks

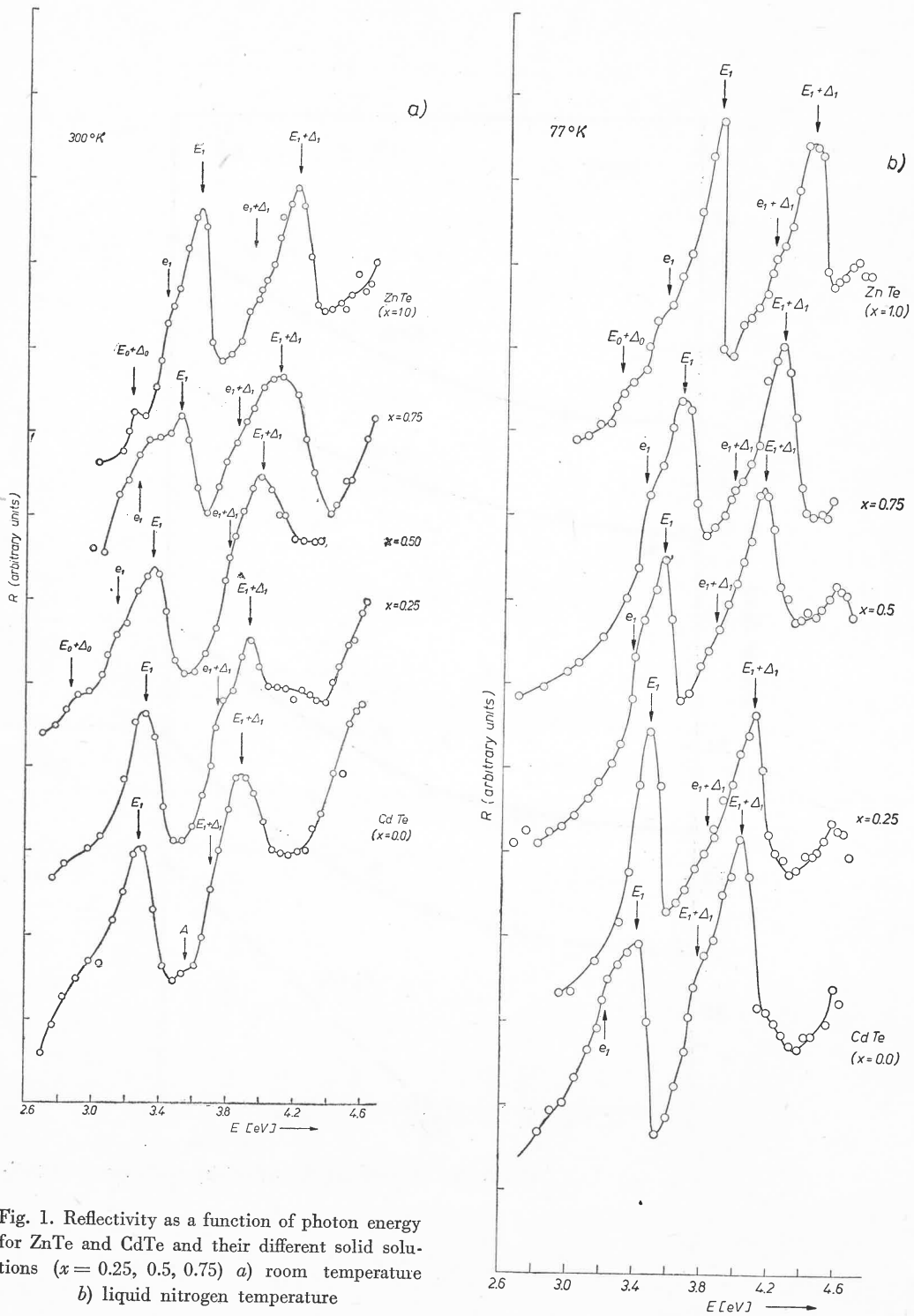


Fig. 1. Reflectivity as a function of photon energy for ZnTe and CdTe and their different solid solutions ( $x = 0.25, 0.5, 0.75$ ) a) room temperature b) liquid nitrogen temperature

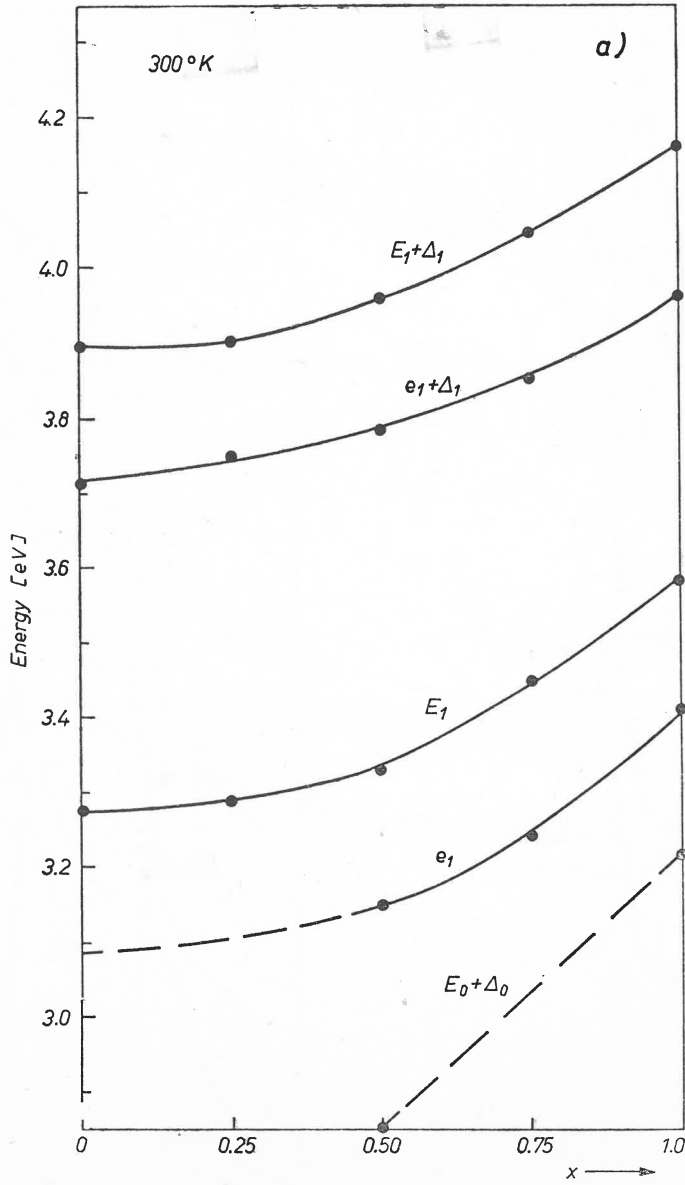
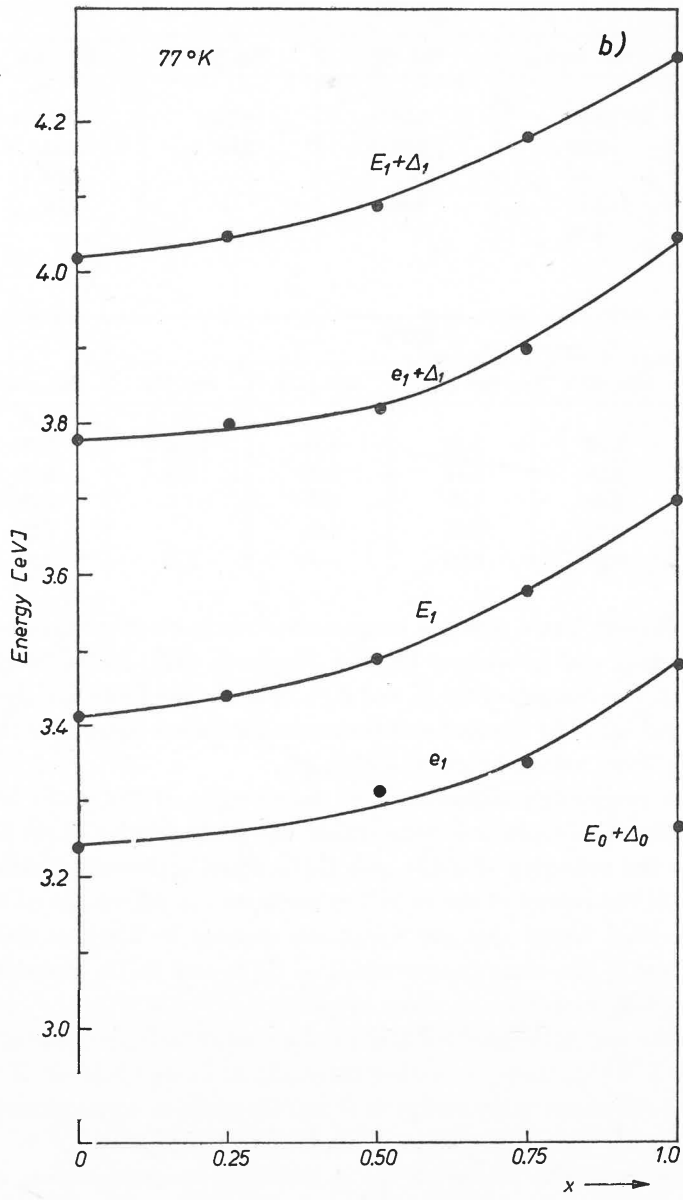


Fig. 2. Plot of energy of the reflectivity peaks versus composi-



tion x a) room temperature b) liquid nitrogen temperature

TABLE I

Results for CdTe and ZnTe

CdTe						
Transition	300°K			77°		
	this work	Ref. [3]	Ref. [4]	this work	Ref. [3]	
$E_1$	3.28	3.32	3.28	3.41	3.44	
$E_1 + \Delta_1$	3.89	3.88	3.87	4.02	4.01	
$e_1$	—	—	—	3.24	—	
$e_1 + \Delta_1$	3.71	3.63	—	3.78	3.77	
$A$	3.56					
ZnTe						
Transition	300°K				77°K	
	this work	Ref. [3]	Ref. [12]	Ref. [4]	this work	Ref. [3]
$E_1$	3.58	3.58	3.58	3.61	3.70	3.70
$E_1 + \Delta_1$	4.16	4.14	4.15	4.18	4.27	4.28
$e_1$	3.40	3.41	3.40		3.48	3.48
$e_1 + \Delta_1$	3.96	3.96	3.95		4.05	4.05
$E_0 + \Delta_0$	3.20	3.26	—	3.18	3.27	

measured both at room liquid nitrogen temperatures are in excellent agreement with values obtained by Cardona and Greenaway [3] and Niculescu [12], and with electro-reflection data (see Table I). The energies of the  $E_1$  and  $E_1 + \Delta_1$  peaks for CdTe are also in conformity with the results published by Cardona and Greenaway, but some energies of the  $e_1$  and  $e_1 + \Delta_1$  thresholds differ from values obtained earlier [3].

Finding the composition-dependence of the energies of the peaks in the reflection spectrum for ZnTe—CdTe solid solutions enables the determination of the relation between the structure in the reflection of ZnTe and CdTe taken separately. Taking into account the dependence of the energy of the reflection peaks on the percentage of the composition (Fig. 2), it has been found that the transitions denoted by Cardona and Greenaway as  $E_1$  and  $E_1 + \Delta_1$  are of the same type as those in CdTe and ZnTe. However, the problem of the  $e_1$  and  $e_1 + \Delta_1$  transitions is more involved.

Apart from the  $e_1 + \Delta_1$  threshold of 3.77 eV observed in CdTe by Cardona and Greenaway [3] (they quoted 3.78 eV), there is another threshold of energy 3.24 eV at liquid nitrogen temperature. The difference in the energy of these two peaks is approximately equal to the spin-orbit splitting for the valence band at the  $L$  point ( $2/3 \Delta_0$ ).

The dependence of the energy of the  $e_1$  threshold on composition shows that the threshold of energy 3.24 eV in CdTe is a transition of the same kind as the threshold 3.48 eV in ZnTe (Fig. 2b). Hence, it may be assumed that the 3.24 eV threshold in CdTe is an  $e_1$  transition.

In the reflectivity spectra of some CdTe specimens at room temperature, very low thresholds of energies of about 3.71 and 3.56 eV are observed. From the dependence of



$LK$ ,  $LW$ ,  $LU$  directions (Fig. 3). In order to be able to say anything about the results obtained earlier and the new data presented here, the following four eventualities should be considered:

a) The  $E_1$  and  $E_1 + \Delta_1$  transitions occur at the  $L$  point of the Brillouin zone or at the nearby  $\Delta$  point, whereas the  $e_1$  and  $e_1 + \Delta_1$  transitions are associated with hyperbolic excitons of the  $L$  or  $\Delta$  points.

b)  $E_1$  and  $E_1 + \Delta_1$  are transitions at the  $L$  point and  $e_1$  and  $e_1 + \Delta_1$  are transitions at the  $\Delta$  point, which is so distant from the  $L$  point that the difference in energy of the valence and conduction bands of these points equals about 0.15 eV (this is the observed energy difference).

c)  $E_1$  and  $E_1 + \Delta_1$  are transitions at the  $L$  point or at a very close  $\Delta$  point, whereas  $e_1$  and  $e_1 + \Delta_1$  are transitions at a  $\Delta$  point lying on the  $FX$  or  $FK$  direction.

d)  $E_1$  and  $E_1 + \Delta_1$  are transitions at the  $L$  point or at a very close  $\Delta$  point, whereas  $e_1$  and  $e_1 + \Delta_1$  are transitions at one of the singularities lying on the  $LW$  ( $Q$  point),  $LU$  or  $LK$  directions.

TABLE II

Temperature coefficient for ZnTe, CdTe and their solid solutions Zn Cd<sub>1-x</sub>Te in (10<sup>-4</sup> eV/°C)

Transition	CdTe $x = 0$	$x = 0.25$	$x = 0.50$	$x = 0.75$	ZnTe $x = 1$
$E_1$	5.9	6.9	7.3	6.4	5.9
$E_1 + \Delta_1$	5.9	6.9	6.9	5.9	5.9
$e_1$	—	—	—	5.0	3.2
$e_1 + \Delta_1$	3.2	2.3	1.8	2.3	4.1
$E_0 + \Delta_0$	—	—	—	—	2.3

TABLE III

Spin-orbit splitting in eV for transitions  $E_1$  and  $e_1$  in ZnTe, CdTe and their solid solutions Zn Cd<sub>1-x</sub>Te for temperature of liquid nitrogen

Transition	CdTe $x = 0$	$x = 0.25$	$x = 0.50$	$x = 0.75$	ZnTe $x = 1.0$
$E_1$	0.61	0.59	0.60	0.60	0.59
$e_1$	0.53	—	0.51	0.55	0.57

Re a) The  $e_1$  and  $e_1 + \Delta_1$  peaks observed here in the reflection spectra of ZnTe, CdTe and their solid solutions were not seen to appear when the electro-reflection technique of Ref. [5] was applied. This fact speaks for an exciton nature of these maxima. Nonetheless, data now possessed [1] give little grounds for assuming that the  $e_1$  and  $e_1 + \Delta_1$  peaks are transitions associated with hyperbolic excitons of the  $L$  or  $\Delta$  points. The expected binding energy [12] for such excitons in zincblende type materials should not exceed 0.1 eV, and the half-width of spectral lines should not be larger than 0.02 eV. But the  $e_1$  and  $e_1 + \Delta_1$  maxima lie about 0.15 eV below the  $E_1$  and  $E_1 + \Delta_1$  peaks, and their half-widths are estimated



to be approximately 0.15 eV. Moreover, it then appears that the temperature coefficient for these transitions should not differ from the temperature coefficient for interband transitions at the  $L$  or  $A$  point.

Re *b*) Let us now look at the situation for the  $LI'$  direction. Theoretical considerations anticipate either the absence of a singularity beyond the  $L$  and  $A$  points [18–22], or the presence of such a point in the immediate vicinity of the  $L$  point (a  $A$  point) [23]. The energy difference of the transitions at the  $L$  and  $A$  points would then be a few hundredths of an electron-volt.

If we assume, however, that contrary to theoretical predictions there is a  $A$  singularity along the  $LI'$  direction so distant from  $L$  that transitions at that point would be observed

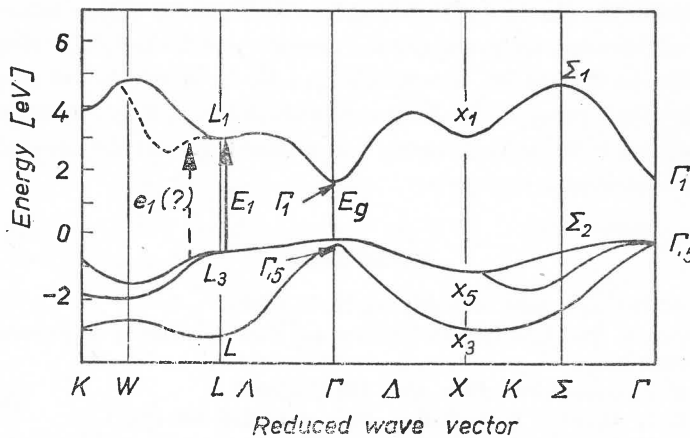


Fig. 4. Simplified diagram of the band structure for CdTe. Dotted lines shown proposed shape of the band structure between point  $L$  and point  $W$  or  $K$ . The transitions are shown by arrows

as another separate peak, it is plausible that the temperature coefficient for this peak is smaller than that for the  $L$  point and larger than for the  $A$  point. Also, the spin-orbit splitting should be smaller than the splitting at the  $L$  point.

The conditions above are fulfilled for the  $e_1$  and  $e_1 + \Delta_1$  maxima (Tables II and III). The assignment of the  $E_1$  and  $E_1 + \Delta_1$  transitions to the  $L$  point of the Brillouin zone and the  $e_1$  and  $e_1 + \Delta_1$  to the  $A$  point of this zone contradicts the calculations made by Brust *et al.* [17] for germanium. It also disagrees with the assignment proposed by Cardona and Greenaway [3] on the basis of paper [17] for the reflection peaks in the spectra of group II–VI compounds.

Re *c*) The shapes of the valence and conduction bands for ZnTe and CdTe in the  $\Gamma X$  and  $\Gamma K$  directions have been derived theoretically, and computations do not corroborate the existence of a singularity of transition energy of about 3.5 eV along these directions in the vicinity of the  $\Gamma$  point.

Re *d*) Because the energy differences between conduction and valence bands at the  $K$  and  $W$  points of the Brillouin zone (data concerning the  $U$  point are unavailable) are greater than the energy difference at the  $L$  point, the existence of singularities along these directions would be associated with the appearance of a local minimum in the conduction

bands in these directions (Fig. 4). Figure 4 depicts the proposed shape of the band on the example of the  $LW$  direction ( $Q$  singularity). Of course, this may be translated to any other point of, say, the  $LK$  or  $LU$  directions.

The appearance of a local minimum in the conduction band at some running point along any one of the directions leading from the  $L$  point has not yet been confirmed by any calculations or experiments. Obviously, this suggestion must give rise to considerable doubts. Notwithstanding this, transitions at the proposed points of the Brillouin zone would possess properties like those found in this work for  $e_1$  and  $e_1 + \Delta_1$ . Out of the possibilities considered here, experimental facts seem to point to the one labelled  $d$ ), but only subsequent detailed studies will be able to give a final answer to these problems.

The author takes the pleasure of thanking Docent W. Girit of the Institute of Physics, Polish Academy of Sciences, for preparing the samples and for helpful fruitful discussion. Thanks are also due to Docent W. Wardzyński and Dr A. Mycielski for valuable remarks during the writing of this paper, to Dr Z. Kossakowska-Kisiel and K. Schab, M.Sc., for their aid in the performance of the measurements and to Mrs J. Kawka for her part in computations on a UMC-1 electronic computer.

#### REFERENCES

- [1] For example J. S. Phillips, *Solid State Physics*, **18**, 55 (1966).
- [2] D. L. Greenaway, G. Harbeke, *Optical Properties and Band Structure of Semiconductors*, Pergamon Press, Oxford 1968.
- [3] M. Cardona, D. L. Greenaway, *Phys. Rev.*, **131**, 98 (1963).
- [4] M. Cardona, K. L. Shaklee, F. H. Pollak, *Phys. Rev.*, **145**, 696 (1967).
- [5] K. E. Shaklee, *Thesis*, Brown University 1969.
- [6] M. Cardona, F. H. Pollak, K. L. Shaklee, *Proc. Internat. Conf. Phys. Semiconductors Kyoto, 1966*; *J. Phys. Soc. Japan*, **21**, 89 (1966).
- [7] U. Gerhardt, *Phys. Rev. Letters*, **15**, 401 (1965); *Phys. Status Solidi*, **11**, 801 (1965).
- [8] M. Cardona, F. H. Pollak, *Bull. Amer. Phys. Soc.*, **12**, 101 (1967).
- [9] F. H. Pollak, M. Cardona, K. L. Shaklee, *Phys. Rev. Letters*, **16**, 442 (1966).
- [10] J. Tauc, A. Abraham, *Proc. Internat. Conf. Semiconductor Physics, Prague 1960* (p. 375); *J. Phys. Chem. Solids*, **20**, 190 (1961).
- [11] E. Schmidt, *Phys. Status Solidi*, **27**, 57 (1968).
- [12] D. Niculescu, *J. Phys. C*, **1**, 804 (1968).
- [13] R. R. Gałazka, A. Kisiel, *Phys. Status Solidi*, **34**, 63 (1969).
- [14] D. Brust, J. C. Phillips, F. Bassani, *Phys. Rev. Letters*, **9**, 94 (1962).
- [15] F. M. Pollak, *Proc. Internat. Conf. II-IV Compounds*, Providence 1967, W. A. Benjamin, Inc., New York 1967 (p. 552).
- [16] F. Herman, R. L. Kortum, C. D. Kuglin, *Bull. Amer. Phys. Soc.*, **12**, 341 (1967).
- [17] F. Herman, R. L. Kortum, C. D. Kuglin, J. L. Shay, *Proc. Internat. Conf. II-VI Compounds*, Providence 1967, W. A. Benjamin, Inc., New York (p. 503).
- [18] I. L. Shay, W. E. Spicer, F. Herman, *Phys. Rev. Letters*, **13**, 649 (1967).
- [19] J. Treusch, P. Eckelt, O. Madelung, *Proc. Internat. Conf. II-VI Semiconducting Compounds*, Providence 1967, W. A. Benjamin, Inc., New York 1967.
- [20] N. L. Cohen, T. K. Bergstresser, *Phys. Rev.*, **141**, 789 (1966).
- [21] Z. Dziuba, *J. Electrochem. Soc.*, **116**, 104 (1969).
- [22] U. Fano, *Phys. Rev.*, **124**, 1866 (1961).
- [23] D. T. E. Marple, H. Ehrenreich, *Phys. Rev. Letters*, **8**, 87 (1962).