



VALENCE BAND STRUCTURE OF PbTe

A. Crocker, L. Rogers

► To cite this version:

A. Crocker, L. Rogers. VALENCE BAND STRUCTURE OF PbTe. Journal de Physique Colloques, 1968, 29 (C4), pp.C4-129-C4-132. 10.1051/jphyscol:1968418 . jpa-00213622

HAL Id: jpa-00213622

<https://hal.science/jpa-00213622>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

VALENCE BAND STRUCTURE OF PbTe

A. J. CROCKER and L. M. ROGERS

Zenith Radio Research Corporation (U. K.) Ltd., Stanmore, Middlesex

Résumé. — Cet article de revue couvre notre travail des dernières années sur le PbTe et l'alliage semiconducteur $\text{Cd}_x\text{Pb}_{1-x}\text{Te}$. Il montre comment les mesures des propriétés de transport et des propriétés optiques de ces matériaux confirment :

1) Le modèle à deux bandes de valence pour PbTe dans lequel la bande principale de faible masse est fortement non parabolique et la bande secondaire de forte masse est parabolique.

2) La valeur d'environ 1/2 du facteur d'anisotropie de Hall de la bande de valence principale dans le cas de PbTe de très forte densité de porteurs à basse température.

Abstract. — This paper is a review article covering our work in recent years on PbTe and the alloy semiconductor $\text{Cd}_x\text{Pb}_{1-x}\text{Te}$. It shows how measurements of the transport and optical properties of these materials support (1) the two valence band model for PbTe in which the principal light mass band is highly non-parabolic and the secondary heavy mass band is parabolic and (2) a value for the Hall-anisotropy factor of the principal valence band, in the case of extremely high carrier density PbTe at low temperatures, of about 1/2.

Experimental determination of the band structure of PbTe in the neighbourhood of the forbidden gap.

Recently we have reported measurements of the transport properties of PbTe [1, 2] and $\text{Cd}_x\text{Pb}_{1-x}\text{Te}$ [3] which strongly support a two valence band model for these materials. In this model the principal light mass band (band 1) is highly non-parabolic with energy extrema located where the $\langle 111 \rangle$ directions in k -space intersect the Brillouin zone boundary and the heavy mass band (band 2) is parabolic for temperatures and carrier concentrations normally encountered. Since the heavy mass band in PbTe is populated only at high temperatures, direct information concerning its structure has not been forthcoming.

Recent band structure calculations [4, 5] suggest that one might find a second valence band in the lead chalcogenides at the Σ points in the reduced zone i. e. midway along the $\langle 110 \rangle$ directions, the energy separation between this band and the principal valence band at L being smallest for PbTe and largest for PbSe. Our experiments at least partially support these calculations. We have found no evidence of heavy hole conduction in PbSe but strong evidence in PbTe.

The direct energy gap in PbTe had previously been found to increase with increasing temperature at the expense of the energy separation between valence band edges. The effect could be reversed under hydrostatic pressure. This inspired us to study alloy systems based on PbTe in which the energy gap was

known to increase with alloying e. g. $\text{Cd}_x\text{Pb}_{1-x}\text{Te}$. If the increase in the forbidden gap was again at the expense of the energy separation between valence band edges then the heavy mass valence band might be heavily populated at low temperatures. Direct

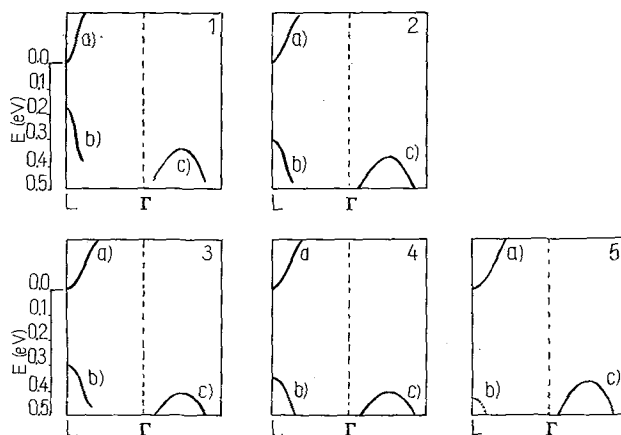


FIG. 1. — Relative energy separations between bands in the neighbourhood of the forbidden gap with respect to the conduction band for PbTe and $\text{Cd}_x\text{Pb}_{1-x}\text{Te}$ at 0 °K and 300 °K.

- | | |
|-----------------------------|----------------------------|
| a) Conduction band. | b) Principal valence band. |
| c) Heavy mass valence band. | |
| 1) $x = 0.00$ | $T = 0^\circ\text{K.}$ |
| 2) $x = 0.03$ | $T = 0^\circ\text{K.}$ |
| 3) $x = 0.00$ | $T = 300^\circ\text{K.}$ |
| 4) $x = 0.03$ | $T = 300^\circ\text{K.}$ |
| 5) $x = 0.11$ | $T = 300^\circ\text{K.}$ |

information concerning the structure of the band could then be obtained.

We found that the above actually happened in the $\text{Cd}_x\text{Pb}_{1-x}\text{Te}$ alloy system, see figure 1. The heavy mass valence band was nearer to the conduction band at and below room temperature in an alloy containing about 10 mol. % CdTe. We observed with n-type alloys, containing up to 10 mol. % CdTe, that the reduction in mobility and increase in thermoelectric power with alloying was consistent with a small increase in the effective mass associated with the larger forbidden gap. There was no evidence of complex scattering i. e. intra-valley acoustic mode lattice scattering remained dominant. In p-type alloys there was a fairly sharp drop in the Hall mobility and corresponding increase in the thermoelectric power for alloy compositions greater than about 7 mol. % CdTe, and the Hall coefficient was no longer observed to increase with increasing temperature, see figure 2. Assuming that the electrons and holes

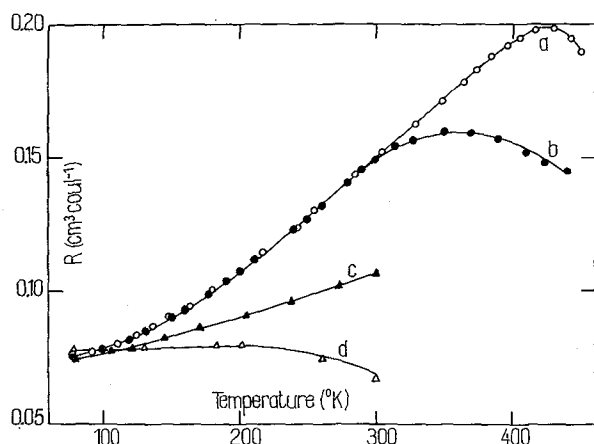


FIG. 2. — Hall coefficient R plotted against temperature for strongly Na-doped $\text{Cd}_x\text{Pb}_{1-x}\text{Te}$ of various compositions.

- a) $x = 0.00$.
- b) $x = 0.027$.
- c) $x = 0.055$.
- d) $x = 0.099$.

were scattered by the same process, the room temperature thermoelectric power for a 10 mol. % CdTe alloy corresponded to an effective density of states mass of 2.0 m and the mobility to a conductivity effective mass of about 0.5 m . These results were most encouraging because they were in excellent agreement with the heavy mass band parameters estimated from (1) our earlier measurements of transport properties [2] and (2) the optical properties as measured by Dixon and Riedl [6]. They were also in agreement with the band structure calculations [4].

It appears that the heavy mass valence band of PbTe consists of 12 valleys with almost equal transverse and longitudinal components of effective mass.

The above meant that the energy separation between valence band edges could now be fairly accurately determined from Hall coefficient measurements on low carrier density PbTe if it was assumed that (1) the effective density of states mass of the heavy holes was independent of temperature and alloying and (2) the principal valence band edge effective mass increased as the forbidden gap. We believed that the light to heavy mass hole mobility ratio μ_1/μ_2 was extremely large below room temperatures in low carrier density PbTe because $\mu_1 \propto T^{-5/2}$ and μ_2 was expected to be

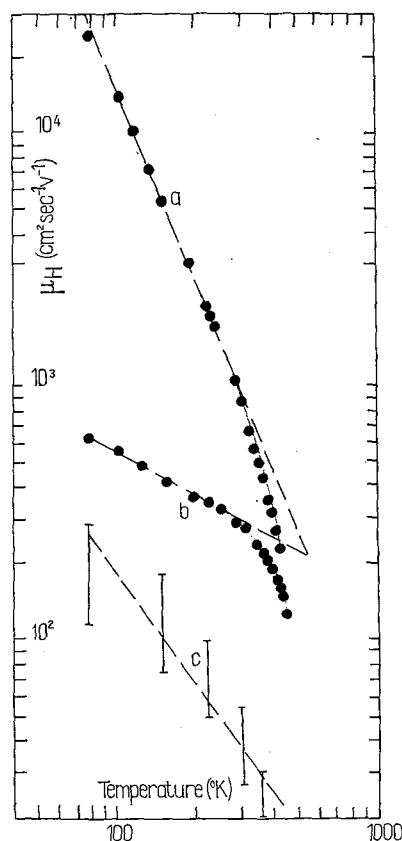


FIG. 3. — Hall mobility μ_H plotted against temperature for undoped and strongly Na-doped p-type PbTe and $\text{Cd}_{0.1}\text{Pb}_{0.9}\text{Te}$

a) PbTe — $p = 4.3 \times 10^{17} \text{ cm}^{-3}$.

Slope of dotted line: $-\frac{5}{2}$ (light mass holes at band edge).

b) PbTe — $p = 1.5 \times 10^{20} \text{ cm}^{-3}$.

Slope of dotted line: $-\frac{1}{2}$ (light mass holes deep inside band).

c) $\text{Cd}_x\text{Pb}_{1-x}\text{Te}$ — $x = 0.11 \pm 0.01$.

$p = 4 \times 10^{17} \text{ to } 8 \times 10^{19} \text{ cm}^{-3}$.

Slope = $-3/2$ (heavy mass holes).

proportional to $T^{-3/2}$ (the reverse was true for high carrier concentrations since $\mu_1 \propto T^{-(1/2 \text{ to } 1)}$ due to non-parabolicity), see figure 3. This considerably simplified the Hall coefficient analysis and the value obtained for the energy separation between valence bands at 0 °K was 0.16 eV [2, 7].

We based our theory on Cohen's [8] dispersion law for energy surfaces with rotation plus reflection symmetry. It followed the lines developed by Kolodziejczak and Zukotynski [9]. Using this theory we could explain most of our results of Hall coefficient, Hall mobility, thermoelectric power and transverse Nernst-Ettingshausen coefficient, but for very high carrier concentration material, at low temperatures, it was necessary to propose that the Hall-anisotropy factor of the principal valence band was about 1/2. To test the theory, which covered the case of extreme degeneracy only, we made use of the established similarity between PbTe and SnTe [10, 11]. When the theory was applied to degenerate SnTe it met with considerable success [12].

In SnTe it is known that the Hall-anisotropy factor of the principal valence band is about 0.6 at low temperatures [13]. Allgaier [14] has shown that a small value of this factor is possible with a highly degenerate Cohen-type-band. He pointed out that such values were more plausible the larger the value of E_F/E_G , and for comparable carrier densities E_F/E_G is much larger at low temperatures in PbTe than in SnTe. However, substitution of the appropriate band parameters for PbTe and SnTe into his formulae gave values close to unity. It should be noted that Allgaier assumed (1) an isotropic relaxation time, and there is evidence from correlation of cyclotron resonance [15] and magneto-resistance [16] data that $\tau_l > \tau_t$ in PbTe at low temperatures (see also the work of Walpole and McWhorter [17]) and (2) that the Cohen relation is valid when $E_F \gg E_G$ (it is recalled that the Cohen theory is mainly a $k \cdot p$ perturbation calculation).

The following is a brief survey of experimental results which tend to support the small value for the Hall-anisotropy factor of the principal valence band of highly degenerate PbTe.

To obtain high carrier density p -type material we always used Na as the dopant. If our ideas regarding the Hall-anisotropy factor were correct then we expected to observe a reduction of about 50 % in the ratio $[\text{Na}]/p^*$ (where the nominal carrier concentration $p^* = 1/R_{77}e$ and the subscript indicates the temperature in °K) when going from the lowest to the highest carrier concentration, and this was

observed, see filled circles in figure 4. The variation from 2 to less than unity could not be explained by

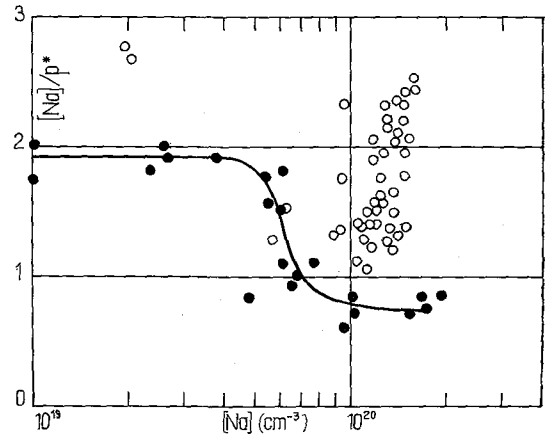


FIG. 4. — The ratio of the sodium concentration (Na) to the nominal carrier concentration plotted against the sodium concentration for PbTe (filled circles) and $\text{Cd}_{0.1}\text{Pb}_{0.9}\text{Te}$ (open circles).

a change in neutrality condition with increasing carrier concentration [18]. We also expected, in our high carrier density material, a significant contribution to the ratio R_T/R_{77} from $(r_1 f_1)_T/(r_1 f_1)_{77}$ (where the Hall-anisotropy factor rf is defined by the weak field formula $R = rf/pe$ and p is the true carrier density). This was because the concentration of light mass holes rapidly decreases with increasing temperature and $r_1 f_1$ is approximately unity for low carrier concentrations. The observed increase in the Hall coefficient with temperature was far greater than expected in view of the small value of the ratio μ_1/μ_2 , the latter being a consequence of the non-parabolicity of the principal valence band and is supported by the Hall mobility data below room temperature for strongly Na doped PbTe and $\text{Cd}_{0.1}\text{Pb}_{0.9}\text{Te}$, see figure 3.

The Hall mobility for strongly Na doped PbTe at low temperatures, where light mass hole conduction dominates, was about half the calculated conductivity mobility according to the non-parabolic band theory. The transverse Nernst-Ettingshausen coefficient also gave a conductivity mobility approximately twice the measured Hall mobility [19]. However, both these results were critically dependent on the energy separation between valence bands at low temperatures i. e. the maximum value that the Fermi energy could take before the heavy mass valence band became populated. We were confident that for the highest carrier concentration studied, namely $p^* = 1.5 \times 10^{20} \text{ cm}^{-3}$, the Fermi energy was about to enter the heavy mass

valence band for the following reasons : (1) the thermoelectric power at 100 °K when plotted against the nominal carrier concentration appeared to reach a minimum at $p^* \approx 10^{20} \text{ cm}^{-3}$, see figure 5, and (2)

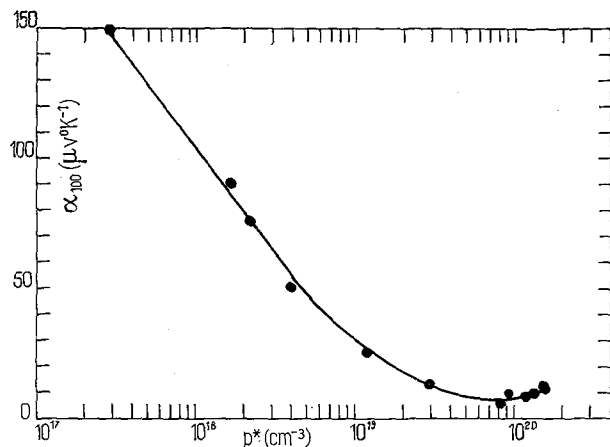


FIG. 5. — Thermoelectric power at 100 °K against nominal carrier concentration for p-type PbTe.

for strongly Na doped $\text{Cd}_x\text{Pb}_{1-x}\text{Te}$ the quantity R_{300}/R_{77} was observed to decrease with increasing x , see figure 6. The maximum light mass hole carrier

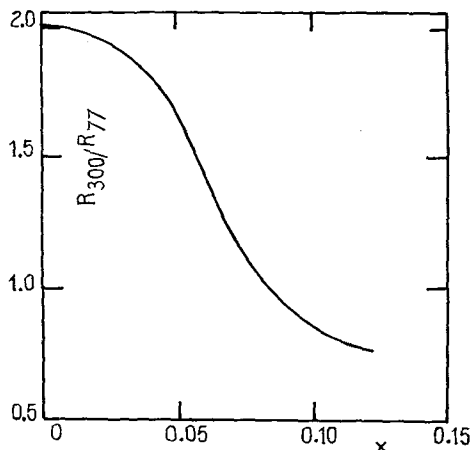


FIG. 6. — The ratio of the Hall coefficient at 300 °K to that at 77 °K plotted against x for strongly Na-doped $\text{Cd}_x\text{Pb}_{1-x}\text{Te}$.

density, which corresponds to a Fermi energy equal to the energy separation between valence bands at 0 °K, was $6 \times 10^{19} \text{ cm}^{-3}$. The small value for the Hall-anisotropy factor accounted for the discrepancy between the calculated and nominal carrier densities [2].

The Hall anisotropy factor of the heavy mass valence band should be about unity for all carrier concentrations. The ratio $[\text{Na}]/p^*$ for Na doped

$\text{Cd}_{0.1}\text{Pb}_{0.9}\text{Te}$ would then be independent of the carrier concentration. Our measurements here have been hampered by the fact that the Na rapidly became electrically neutral following annealing at 800 °C and quenching to room temperature (a process which was necessary to get the CdTe into solution). This meant that the Hall coefficient had to be measured immediately after quenching otherwise it would bear no relation to the sodium concentration. We have been unable to draw definite conclusions from these measurements in view of the large experimental error, see open circles in figure 4.

To summarise, the two valence band model for PbTe can explain the measured transport properties provided the Hall-anisotropy factor of the principal valence band in highly degenerate material is about 1/2. By alloying PbTe with CdTe it has been possible to obtain direct information concerning the heavy mass valence band. It appears that the effective density of states mass of this band is far greater than the conductivity effective mass. This implies a large number of valleys in agreement with the band structure calculations.

References

- [1] CROCKER (A. J.) and ROGERS (L. M.), *Brit. J. Appl. Phys.*, 1967, **18**, 563-73.
- [2] ROGERS (L. M.), *Brit. J. Appl. Phys.*, 1967, **18**, 1227-35.
- [3] ROGERS (L. M.) and CROCKER (A. J.), to be published.
- [4] LIN (P. J.) and KLEINMAN (L.), *Phys. Rev.*, 1966, **142**, 478-89.
- [5] RABII (S.), *Phys. Rev.*, 1968, **167**, 801-8.
- [6] DIXON (J. R.) and RIEDL (H. R.), *Phys. Rev.*, 1965, **138**, A873-81.
- [7] ALLGAIER (R. S.) and HOUSTON (B. B.), Jr., *J. Appl. Phys.*, 1966, **37**, 302-9.
- [8] COHEN (M. H.), *Phys. Rev.*, 1961, **121**, 387-95.
- [9] KOŁODZIEJCZAK (J.) and ZUKOTYNSKI (S.), *Phys. Status Solidi*, 1964, **5**, 145-58.
- [10] ALLGAIER (R. S.) and HOUSTON (B. B.), Jr., 1962, *Proc. 6th Int. Conf. on Physics of Semiconductors*, Exeter, 1962. (London : Institute of Physics and Physical Society, pp. 172-8.)
- [11] DIMMOCK (J. O.), MELNGAILIS (I.) and STRAUSS (A. J.), *Phys. Rev. Letters*, 1966, **16**, 1193-6.
- [12] ROGERS (L. M.), *Brit. J. Appl. Phys. (J. Phys. D)*, 1968, **1**, 845-52.
- [13] HOUSTON (B. B.), ALLGAIER (R. S.), BABISKIN (J.) and SIEBENMANN (P. G.), *Bull. Am. Phys. Soc.*, 1964, **9**, 60.
- [14] ALLGAIER (R. S.), *Phys. Rev.*, 1966, **152**, 808-16.
- [15] NII (R.), *J. Phys. Soc., Japan*, 1964, **19**, 58-66.
- [16] ALLGAIER (R. S.), *Phys. Rev.*, 1960, **119**, 554-61.
- [17] WALPOLE (J. N.), and McWHORTER (A. L.), *Phys. Rev.*, 1967, **158**, 708-18.
- [18] CROCKER (A. J.), *J. Phys. Chem. Solids*, 1967, **28**, 1903-12.
- [19] ROGERS (L. M.), *Brit. J. Appl. Phys. (J. Phys. D)*, 1968, **1**, 1067-70.