

Mercury chalcogenides under pressure

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Abstract. The mercury chalcogenides, HgTe and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, have received considerable attention in recent years because of their use in infrared photon detectors. This article is concerned with some recent experiments on the Γ_6 - Γ_8 band crossover in these systems induced by pressure. It is shown that although the inverted band model is valid for HgTe, the conclusions of the earlier workers on the pressure induced Γ_6 - Γ_8 crossover are erroneous. Experimental results show that it is difficult to observe the band crossover due to an intervening structural phase transition from cubic zinc blend to the cinnabar structure. However pressure experiments on the semiconductor alloy system $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$ clearly indicate this crossover. New results on the zinc blend-cinnabar phase transformation are also presented. The striking behaviour of thermoelectric power in the high pressure cinnabar phase is correlated with the available experimental data on the structurally similar elemental semiconductors like selenium and tellurium.

Keywords. Mercury chalcogenides; narrow band gap semiconductors; high pressure; thermoelectric power

1. Introduction

The mercury chalcogenides HgTe and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystallize in the cubic zinc blend structure. It is now well established that HgTe is a symmetry induced zero gap semiconductor (Verie 1973). Groves and Paul (1963) had proposed that the ordering of the Γ_6 and Γ_8 bands in HgTe is inverted while it is normal in the generically related semiconducting compounds like CdTe. According to this model, the light electron conduction band and the heavy hole valence band, both belonging to Γ_8 with p -symmetry are degenerate at $k = 0$ due to the cubic symmetry of the zinc blend structure. The light hole valence band Γ_6 having S -symmetry lies below the Γ_8 band. The gap $E_g = E_{\Gamma_6} - E_{\Gamma_8}$ is negative in HgTe and has the significance of an optical gap whereas in CdTe it is positive and represents the thermal gap. Figure 1(a) gives a schematic diagram of the band structure near $k = 0$ in HgTe. As the mean atomic number Z decreases when HgTe is alloyed with CdTe, the Γ_6 band moves to higher energies relative to the Γ_8 band. The pseudobinary alloy system $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$ has $E_g = 0$ corresponding to a degeneracy between the Γ_6 and Γ_8 bands at $k = 0$ (figure 1(b)). In the entire zinc blend family of semiconductors it has been experimentally observed that the Γ_6 band moves to higher energies relative to the Γ_8 band with the application of hydrostatic pressure (Paul and Brooks 1963). This implies that in HgTe, the application of pressure could bring about a reversal in the band ordering while the gap opens up in $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$ (figure 1(c)).

The measurements of thermoelectric power (TEP) in HgTe as a function of pressure by Piotrkowski *et al* (1965) were considered crucial in establishing the Groves-Paul model for its energy band structure. These authors argued that the variation of TEP with pressure should be markedly different in the inverted and normal band structures. TEP depends mainly on the effective mass m^* and carrier concentration n through the

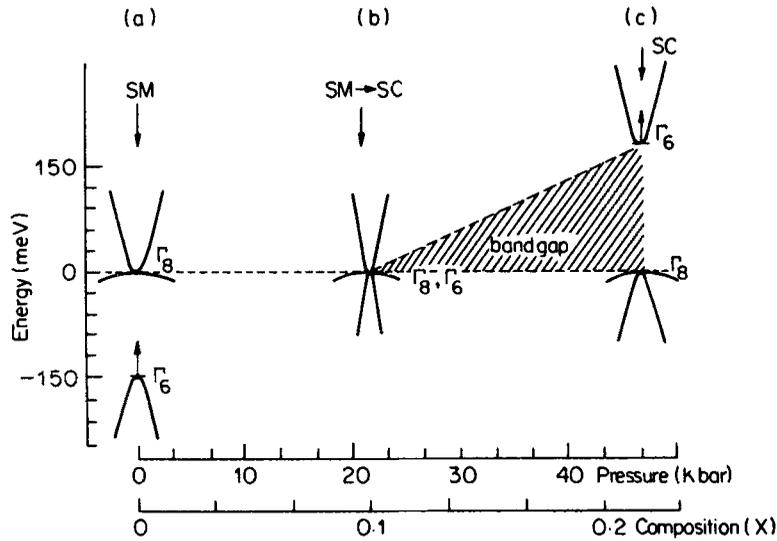


Figure 1. Schematic energy band structure around $k = 0$ in HgTe and $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$.

relation (Ravich *et al* 1970)

$$Q = \frac{2\pi^{2/3} k_B^2 T m^*}{3^{5/3} e \hbar^2 n^{2/3}} (r + 3/2), \quad (1)$$

where r represents the energy dependence of the relaxation time which is expected to be independent of pressure. An important characteristic of the “K.P. interacting” Γ_6 and Γ_8 bands is that the band edge effective mass is directly proportional to E_g (Kane 1957). In an inverted band structure it is clear that m^* , the effective mass in the light electron Γ_8 band, decreases with pressure due to the closing in of the optical gap. Experimentally it has been observed that n also decreases with pressure (Otmezguine *et al* 1970). Thus the TEP in an inverted band structure could either decrease or increase with pressure depending on which of these two effects dominate. On the other hand, in a normally ordered band structure m^* increases with pressure while n decreases due to the opening of the thermal gap E_g . Hence TEP should only increase with pressure. The experimental data of Piotrkowski *et al* (1965) are given in figure 2. TEP is nearly independent of pressure in the low pressure region, whereas it increases rapidly above 12 kbar. This increase was attributed to Γ_6 - Γ_8 crossover.

In this article we provide new evidence to suggest that this crossover cannot be observed in HgTe because of an intervening structural phase transition. A clear indication of this crossover can however be observed in $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$ system. We also present some new data on the zinc blend-cinnabar type structural transformation in both these systems. The anomalous decrease of TEP in the high pressure cinnabar phase strongly suggests that the energy gap decreases with pressure, similar to that observed in structurally related elemental semiconductors like Se and Te.

2. Experimental

The binary tellurides HgTe and CdTe were prepared initially using high purity elements (6N grade). Single crystals of HgTe and $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$ were then grown by a

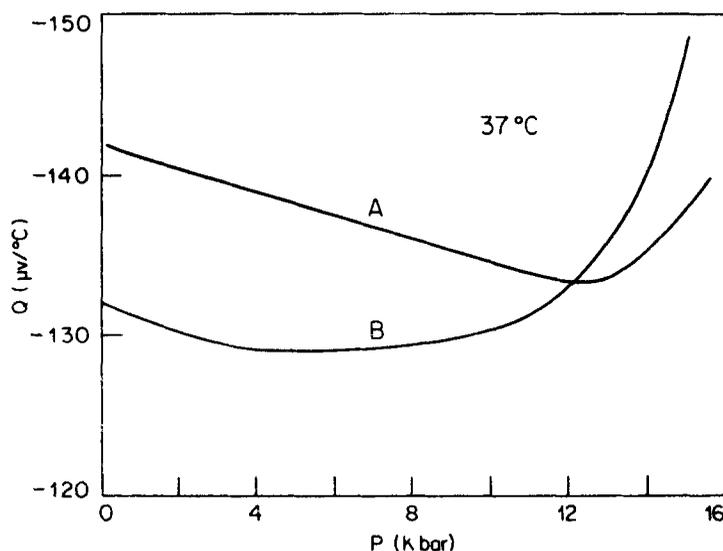


Figure 2. TEP against pressure in HgTe. Curve A: Present data. Curve B: Piotrkowski *et al* (1965).

modified vertical zone melting process (Gopalakrishnan 1981). High pressure experiments were carried out in a conventional piston-cylinder apparatus. The teflon cell technique for TEP measurement and the automatic data acquisition system have been described elsewhere (Reshamwala and Ramesh 1974; Shubha and Ramesh 1976).

3. Results

In figure 2 the present experimental data on TEP versus pressure in a single crystal of HgTe are compared with the earlier measurements of Piotrkowski *et al* (1965). The teflon cell technique with silicone fluid permitted a true hydrostatic environment for the sample. This was essential because of the fact that a uniaxial stress component will lift the degeneracy between the light electron conduction band and heavy hole valence band at the point. TEP increases by $6 \mu\text{V}/^\circ\text{C}$ between 12 and 14.5 kbar whereas the increase is around $20 \mu\text{V}/^\circ\text{C}$ in the earlier work. The decrease of TEP with pressure in the low pressure region is more marked in the present experimental work.

Figure 3 shows a series of isotherms between 40 and 140°C. The main feature here is that the minimum in the TEP versus pressure plot shifts to lower pressures with the increase in temperature.

Figure 4 gives the TEP behaviour of $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$ as compared to that in HgTe as a function of pressure. There is a marked increase in TEP with pressure in $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$ due to the opening of a true gap. The magnitude of TEP changes by $55 \mu\text{V}/^\circ\text{C}$ over a 15 kbar pressure interval. In the case of HgTe the change is around $5 \mu\text{V}/^\circ\text{C}$ in the same pressure region.

The first order phase transformation from the cubic zinc blend to the cinnabar structure is shown in figure 5 for HgTe and in figure 6 for $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$. The equilibrium transformation pressure which is the average of the forward and reverse runs is 14.5 kbar for HgTe. TEP changes sign across the phase transition in both these

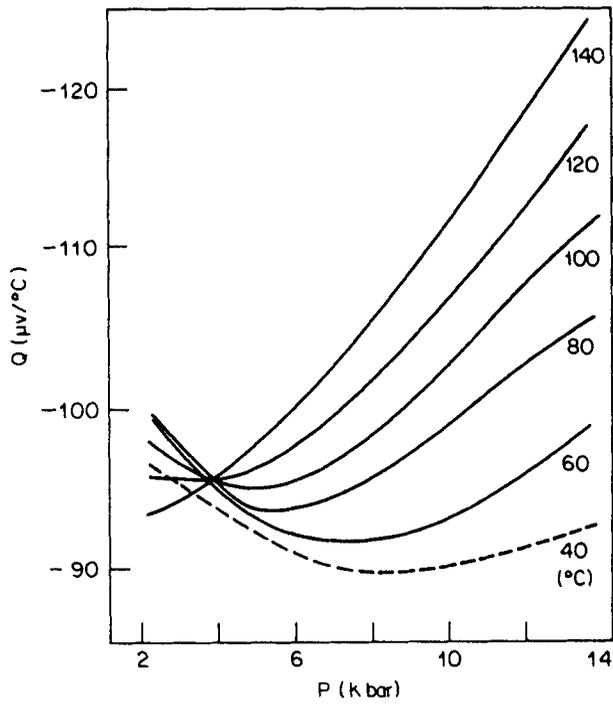


Figure 3. Isotherms of TEP against pressure in HgTe.

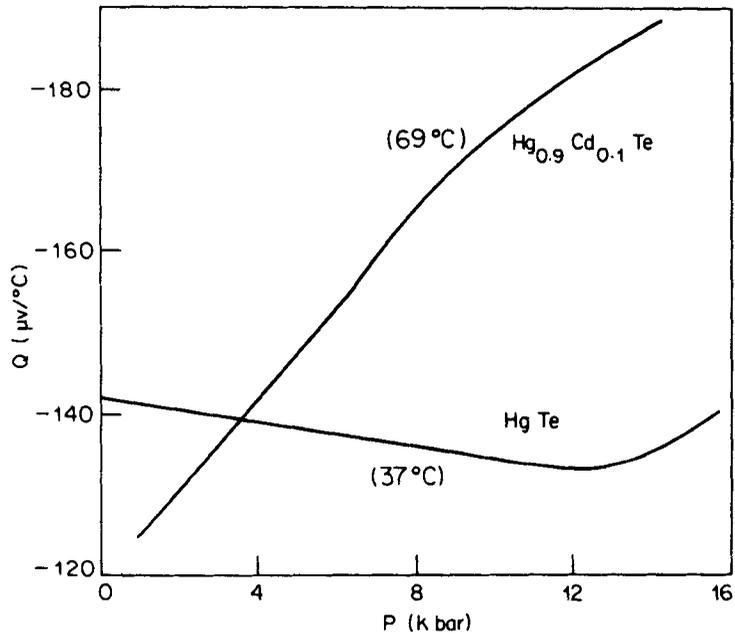


Figure 4. TEP versus pressure in $Hg_{0.9}Cd_{0.1}Te$ and HgTe.

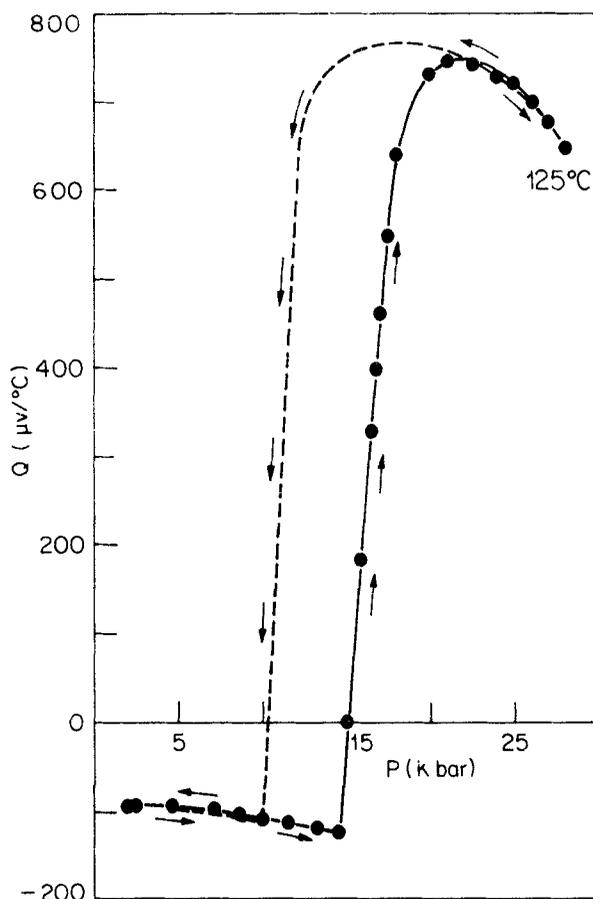


Figure 5. Zinc blend to cinnabar structural transformation in HgTe.

systems. This structural phase transformation was sluggish especially near room temperature and took several hours (24 hours) for the completion of the transition. The transformation was faster (10 hours) at higher temperatures. The important feature in both figures 5 and 6 is the anomalous decrease of T_{EP} with pressure in the cinnabar phase.

4. Discussion

In a system like HgTe which has an inverted band ordering, although the crossover appears as a distinct possibility, our present experimental results show that this does not occur because of an intervening structural phase transformation.

Piotrkowski *et al* (1965) attribute the steep increase in T_{EP} near 14 kbar (curve B in figure 2) to the $\Gamma_6-\Gamma_8$ band crossover. The present data on a single crystal of HgTe (curve A in figure 2) show a marked decrease in the low pressure region while the increase above 12 kbar is less pronounced. This, we believe, is a characteristic behaviour of an inverted band structure and not associated with a band crossover. Since there are two opposing contributions to T_{EP} (equation (1)), it is conceivable that the small

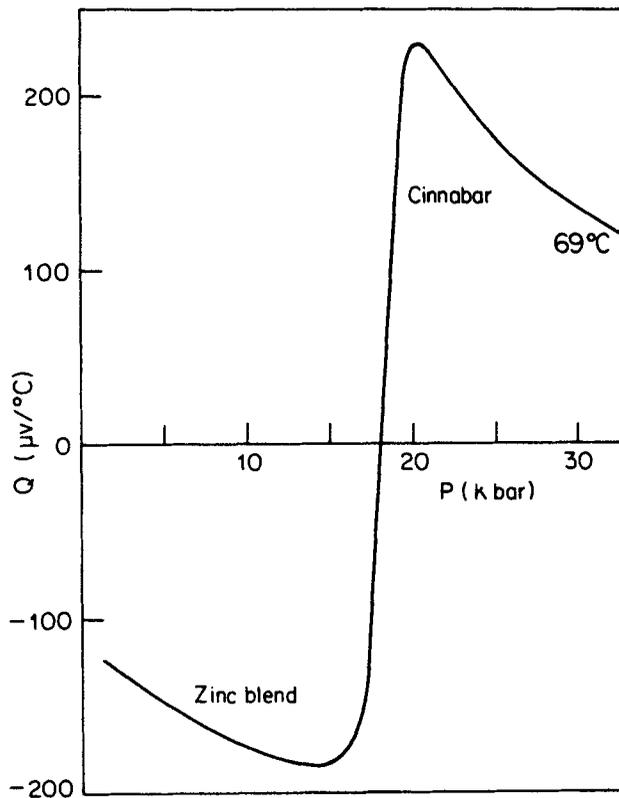


Figure 6. Zinc blend to cinnabar structural transformation in $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$.

increase in TEP near 12 kbar is due to decrease in n with pressure making a dominant contribution over the decrease in m^* . Strong support for this conclusion emerges from a careful analysis of the present data on the pressure and temperature dependence of TEP. Piotrkowski *et al* (1965) give for E_g and dE_g/dP , the values of 190 MeV and 14 MeV/kbar which are consistent with their TEP measurements. It is now well established that these values are too large and more direct measurements (Verie and Martinez 1968) give dE_g/dP as 8 MeV/kbar and E_g at 300°K to be around 150 MeV (Verie and DeCamps 1965). With these values, the Γ_6 - Γ_8 crossover should occur only near 19 kbar pressure. The temperature behaviour of TEP provides further support to this view. It is known that $|E_g|$ decreases with temperature (Dornhaus and Nimtz 1976) so that a combination of temperature and pressure experiments would be useful to detect the Γ_6 - Γ_8 crossover transition. If we analyse, say the 100°K isotherm (figure 3), the increase in TEP beyond 5 kbar pressure would have been interpreted by the previous workers as due to the Γ_6 - Γ_8 crossover. This conclusion turns out to be erroneous for the following reason. The gap E_g at 100°K turns out to be around 113 MeV using the known value of $dE_g/dT \approx 0.5$ MeV/°K (Dornhaus and Nimtz 1976). Since the optical gap E_g closes at the rate of 8 MeV/kbar the crossover should occur only near 14 kbar pressure. We therefore believe that the small increase in TEP with pressure (curve A in figure 2) does not necessarily imply that the crossover transition has occurred. A direct demonstration of the pressure induced Γ_6 - Γ_8 crossover in HgTe is rendered difficult

because of an intervening structural transformation from the zinc blend to the cinnabar type near 14 kbar pressure. We propose that the effect of decrease of n with pressure predominates over that of m^* leading to an increase in TEP with pressure.

Strong and conclusive evidence of Γ_6 - Γ_8 crossover transition comes from a combination of alloying and pressure experiments on $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ system. The marked increase in TEP with pressure in $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$ (figure 4) is only consistent with the energy band model where the gap E_g opens up with the application of pressure. This conclusion is in agreement with the experimental work of Verie and Martinez (1968) who studied the current-voltage relationship in p - n junctions prepared in $\text{Hg}_{0.89}\text{Cd}_{0.11}\text{Te}$ system upto 13.5 kbar pressure. As $X < 0.14$, the p - n junction is ohmic at ambient pressure. For $P > 6$ kbar they exhibit electrical rectification which is a clear demonstration of the band crossover induced by hydrostatic pressure.

The large magnitudes of TEP (figures 5 and 6) in the cinnabar phase suggests that it is a wide gap semi-conductor. A previous study on HgSe has established that the energy gap of the cinnabar structure rapidly decreases with pressure (Ramesh and Shubha 1982). The remarkable variation of TEP in the cinnabar phase can be correlated with the pressure-induced changes in its structure. The cinnabar structure is composed of Hg - Te chains helically wound round the C -axis. The bonding is covalent within the chain while the chains are held together in a hexagonal lattice by a weak mixture of electronic and van der Waal's forces. It may be expected that under pressure, the spacing in the a -direction shrinks much faster than that along the c -direction. This is similar to the observed lattice parameter variation under pressure in structurally similar elemental semiconductors Se and Te (Keller *et al* 1977). Thus, under pressure, the interaction between the helical chains becomes stronger leading to a reduction in the energy gap. Strong support for this hypothesis can be found in the band structure of crystalline selenium (Treich and Sandrock 1966). Here the smallest gap occurs in the neighbourhood of the H -point corresponding to a crystallographic axis which is neither parallel nor perpendicular to C -axis. The band structure along the direction H - K in the Brillouin zone is mainly determined by the interaction between the helical chains. We believe that the energy gap reduction with pressure and hence the decrease of TEP with pressure in the cinnabar phase of HgSe (Ramesh and Shubha 1982), HgTe , $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$ and in Se and Te (Balchan and Drickamer 1961) have a common origin.

5. Conclusions

Pressure and temperature experiments on HgTe have shown that there is no Γ_6 - Γ_8 band crossover while in $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$ it could be easily observed. The anomalies in the TEP behaviour in the cinnabar phase have been shown to arise from a structural origin.

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