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Pressure-induced band cross-over in $Pb_{1-x}Sn_xTe$

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Abstract. Resistivity and thermoelectric power studies have been carried out on two semiconductor alloy systems viz $Pb_{0.8}Sn_{0.2}Te$ and $Pb_{0.6}Sn_{0.4}Te$ up to 35 kbar pressure. Thermoelectric power and resistivity data on $Pb_{0.8}Sn_{0.2}Te$ indicate that the energy gap $E_g = E_{L_6^-} - E_{L_6^+}$ decreases with pressure resulting in a zero gap state near 35 kbar pressure. TEP studies on the alloy system $Pb_{0.6}Sn_{0.4}Te$ provide direct evidence for a pressure induced $L_6^- \rightarrow L_6^+$ cross over transition.

Keywords. Thermoelectric power; band cross-over; narrow gap semi-conductors; lead tin telluride.

1. Introduction

The semiconducting alloy system $Pb_{1-x}Sn_xTe$ has received considerable attention in recent years in view of its importance as an infrared detector material and also as a thermoelectric material (Ravich *et al* 1970). It is known that these solids are semiconductors having a rocksalt crystal structure throughout the range $0 \leqslant x \leqslant 1$. Band structure calculations (Conklin *et al* 1965) show that the valence and conduction band extrema in the Pb salts occur at the L-point in the Brillouin zone. In PbTe the conduction band is L_6^- while L_6^+ is the valence band. Since these bands have only a two-fold spin degeneracy, it is a semiconductor. Due to relativistic effects, alloying with SnTe results in a reduction of the energy gap $E_g = E_{L_6^-} - E_{L_6^+}$ (Verie 1973). According to the band model proposed by Dimmock *et al* (1966), E_g decreases upon alloying and beyond a certain concentration the valence and conduction bands cross over and exchange roles. The application of pressure also leads to a reduction of the principal energy gap E_g. Akimov *et al* (1978) used galvanomagnetic and oscillatory effects as a means for determining the energy band parameters of $Pb_{1-x}Sn_xTe$ alloys with $x = 0{\cdot}18$ and $0{\cdot}23$ under pressure. These authors found that there is a pressure-induced transition to the zero gap state in these alloy systems. A considerable increase in the hole relaxation time was observed on transition to the zero gap state under pressure which was attributed to a reduction in the density of states and an increase in the Fermi energy. These authors also found that at a particular pressure there is an inversion in the band structure.

In this paper we report some new measurements of TEP and resistivity behaviour of the alloy systems $Pb_{0.6}Sn_{0.4}Te$ and $Pb_{0.8}Sn_{0.2}Te$ upto 35 kbar pressure. The pressure behaviour of TEP in $Pb_{0.6}Sn_{0.4}Te$ gives clear evidence for a pressure-induced L_6^- to L_6^+ cross-over near 13 kbar at ambient temperature, whereas the $Pb_{0.8}Sn_{0.2}Te$ system approaches a zero gap state near 35 kbar. The temperature behaviour of TEP and resistivity at different pressures strongly suggest that these systems are degenerate semiconductors.

2. Experimental procedure

Samples of $Pb_{0.8}Sn_{0.2}Te$ and $Pb_{0.6}Sn_{0.4}Te$ were prepared by taking the stoichiometric ratios of high purity PbTe and SnTe and melting the mixture. The mixture was homogenized by repeated melting. Crystals of these samples were then grown using the Bridgman technique. The techniques for high resolution TEP measurement in a piston-cylinder apparatus under controlled conditions of both temperature and temperature gradient have been described elsewhere (Shubha and Ramesh 1986a,b). The experimental data were collected in the teflon cell arrangement with silicone fluid as the pressure-transmitting medium (Shubha and Ramesh 1986a).

3. Results

3.1 $Pb_{0.6}Sn_{0.4}Te$

The variation of TEP and resistivity with pressure near ambient temperature is shown in figure 1. The samples are *p*-type and TEP exhibits a marked pressure dependence with a minima near 13 kbar. Resistivity, however, continuously decreases with pressure with no feature near 13 kbar. We attribute the minima in the TEP vs pressure graph to the pressure induced $L_6^- - L_6^+$ cross-over transition. The isotherms of TEP vs pressure upto 150 C are given in figure 2. It may be noted that the pressure corresponding to the minimum in the TEP vs pressure plot shifts to higher values with increase in temperature. This is related to the temperature variation of the principal energy gap $E_g = E_{L_6^+} - E_{L_6^-}$ which will be discussed later. In contrast, the isotherms of resistivity (figure 3) do not show any features near the pressure corresponding to the band cross-over.

The temperature behaviour of the resistivity at different pressures for the

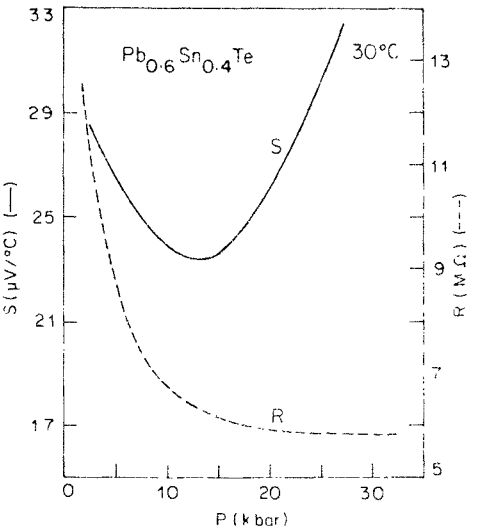

Figure 1. Resistivity (dashed curve) and thermopower (solid line) vs pressure in $Pb_{0.6}Sn_{0.4}Te$.

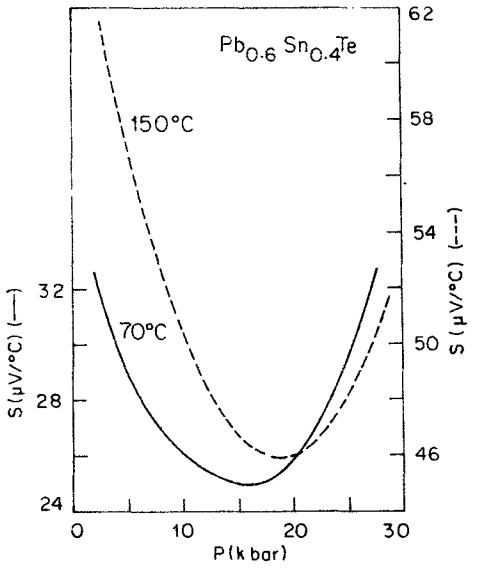

Figure 2. Isotherms of TEP variation with pressure.

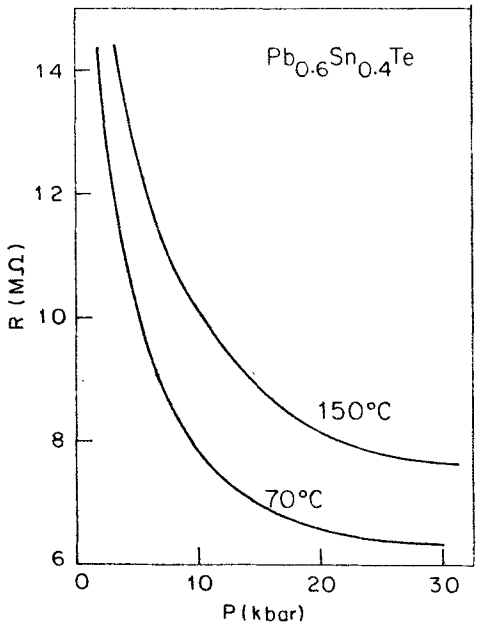

Figure 3. Isotherms of resistivity variation with pressure.

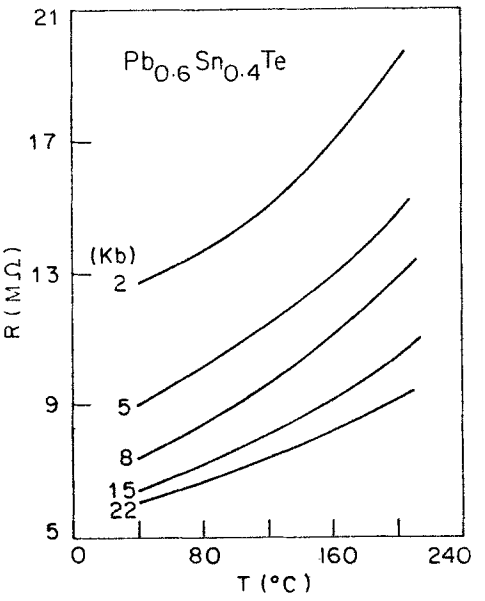

Figure 4. Resistivity vs temperature at different pressures.

$Pb_{0.6}Sn_{0.4}Te$ system is given in figure 4. The positive temperature coefficient of resistivity clearly points out that the samples under study are degenerate semiconductors. The positive temperature coefficient of TEP (dashed curves in figure 5) also supports this view.

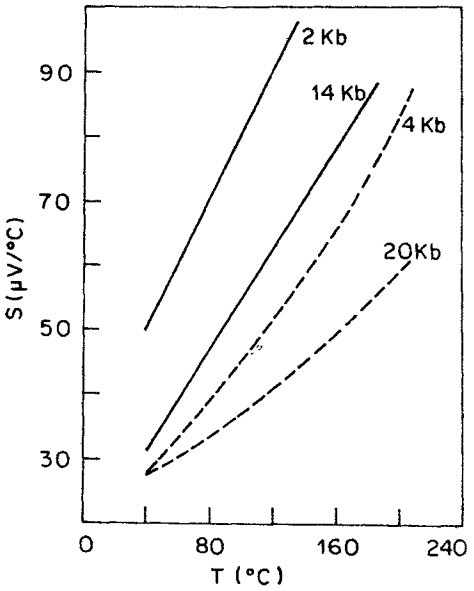

Figure 5. TEP variation with temperature in $Pb_{0.6}Sn_{0.4}Te$ (dashed lines) and $Pb_{0.8}Sn_{0.2}Te$ (solid lines).

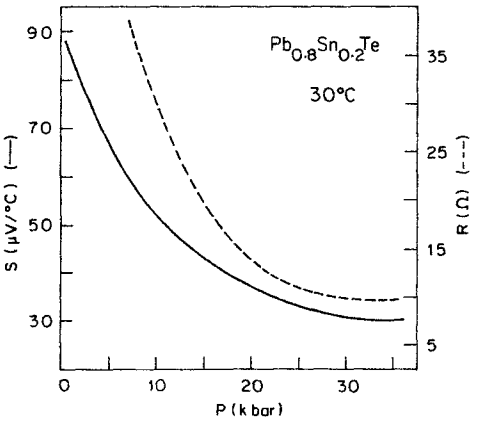

Figure 6. Resistivity (dashed curve) and thermopower (solid line) vs pressure in $Pb_{0.8}Sn_{0.2}Te$.

3.2 $Pb_{0.8}Sn_{0.2}Te$

Figure 6 presents the TEP and resistivity data for $Pb_{0.8}Sn_{0.2}Te$ as a function of pressure. Both TEP and resistivity continuously decrease with pressure upto 35 kbar. This alloy system has a higher energy gap $E_g = 220$ MeV as compared to the $Pb_{0.6}Sn_{0.4}Te$ system ($E_g \simeq 110$ MeV) and a comparison with the TEP data in figure 1 suggests that in this system a zero gap state is reached around 35 kbar. The band cross-over would occur at a higher pressure. The temperature behaviour of TEP (solid line in figure 5) differs from that of $Pb_{0.6}Sn_{0.4}Te$ (dashed curves in figure 5) in which it is highly linear. The isobars at 2 and 14 kbars are well separated from each other compared to the isobars at 4 and 20 kbars of $Pb_{0.6}Sn_{0.4}Te$ because in the latter case TEP is a double-valued function of pressure due to the band cross-over. The temperature behaviour of resistivity is very similar to that in the $Pb_{0.6}Sn_{0.4}Te$ system (figure 4).

4. Discussion

It is now well established that lead chalcogenide alloys exhibit a pressure-induced semiconductor-semiconductor transition corresponding to the $L_6^- - L_6^+$ cross-over. Earlier resistivity measurements at different temperatures under pressure did not permit clear conclusions about a band-crossing induced by pressure (Melngailis *et al* 1970). Strong evidence for a cross-over however came by the observation of the emission wave length λ of a PbTe-rich alloy diode laser subjected to high pressures at 77°K (Martinez 1973c). The emission wavelength increases upto 20 μm, followed by an extinction with increasing pressure and then by the reappearence of laser emission

in the high pressure region. These results are in complete conformity with the band model proposed by Dimmock *et al* (1966). According to this model, dE_g/dP changes sign from negative to positive values in going from an inverted band ordering to a normal situation.

The present TEP and resistivity measurements under pressure can also be understood on the basis of the Dimmock model. The temperature behaviour of both resistivity and TEP (figures 4 and 5) imply that the semiconducting samples are highly degenerate. Further, the Hall effect measurements under pressure (Martinez 1973b) clearly show that the carrier concentration is more or less independent of pressure. Thus the resistivity variation with pressure is the inverse of the mobility variation. Martinez (1973b) noted that the pressure dependence of the mobility is quite different for *n*- and *p*-type samples of equivalent carrier concentrations. In particular, for *p*-type samples the mobility does not reach the expected maximum value near $E_g = 0$ and gets shifted considerably towards the negative gaps i.e. towards the region where the band ordering is reversed. Thus the resistivity continues to decrease with pressure even after the cross-over transition (figures 1 and 3).

In contrast to the resistivity behaviour TEP variation gives clear evidence for the band cross-over in the $Pb_{0.6}Sn_{0.4}Te$ system (figures 1 and 2). We interpret these results using the TEP expression appropriate to metallic samples as these systems are highly degenerate. Then the variation of TEP with pressure mainly stems from the dependence of the Fermi energy E_F on the energy gap with the condition that the carrier concentration remains unchanged with pressure. Model calculations on the behaviour of Fermi energy for a given number of carriers, when the gap is varying (either due to pressure or alloying) in Kane type band structures have been performed by Martinez (1973a). These calculations show that the Fermi energy E_F passes through a maximum at $E_g = 0$. Figure 7 gives the schematic diagram of band inversion induced by pressure appropriate to lead salts. Figure 8 shows the variation of Fermi level as a function of E_g (or pressure) for a given carrier concentration. It is clear that as TEP is inversely related to E_F, TEP should exhibit a minimum near the band cross-over transition. At ambient pressures $Pb_{0.6}Sn_{0.4}Te$ has the band ordering with L_6^- as the conduction band and L_6^+ as the valence band. Since $E_g = E_{L_6^-} - E_{L_6^+}$ decreases with pressure (dE_g/dP is negative), TEP also decreases with

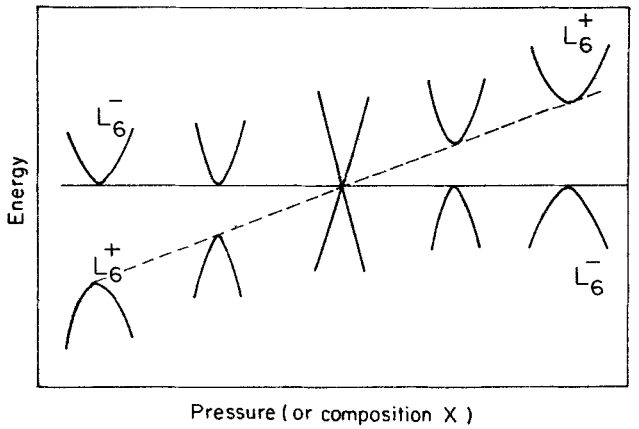

Figure 7. Schematic energy band structure for $Pb_{1-x}Sn_xTe$.

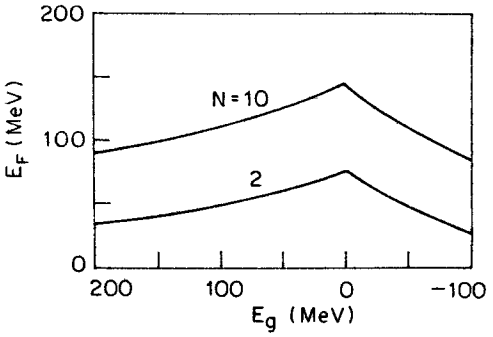

Figure 8. Variation of Fermi energy as a function of E_g for a given carrier concentration N (in 10^{18} cm^{-3} units).

pressure. After the cross-over dE_g/dP becomes positive and TEP increases with pressure. Using the reported values of $E_g \approx 110$ MeV at 300°K and $dE_g/dP = -8{\cdot}6$ MeV/kbar (Martinez 1973a), E_g should become zero near 12·8 kbar. This correlates well with the present experimental observation of the minimum in TEP vs pressure curve near 13 kbar (figure 2) which we attribute to the band cross-over transition. The shift in the pressure corresponding to the minimum with temperature (figure 2) can be understood by noting that the temperature coefficient of E_g is positive for the lead rich alloys (Dimmock *et al* 1966). With increasing temperature E_g increases and therefore the pressure required to reach the zero gap state should also increase. Thus we can account for the shift towards higher pressures in the TEP vs pressure plot with increasing temperature.

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