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DISCLAIMER

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Introduction

Tin telluride is an outstanding example of a low carrier density superconductor. Extensive work has been carried out on the electrical and superconducting properties of this material (1), but our knowledge of its electronic band structure is incomplete. In order to remedy this deficiency, we have measured the low temperature heat capacity of SnTe for various carrier densities and for several doping techniques. Our results for self-doped and Ag-doped samples suggest the presence of two different bands, with two different effective masses. Data for Mn-doped samples indicate an ordering of the Mn spins.

Experimental

In the present work only p-type SnTe was investigated. Two types of samples were used (2): self-doped samples, represented by the formula

$Sn_{1-x}Te$, and samples in which non-divalent impurities (Mn or Ag) were substituted for Sn.

Self-doped samples were prepared by sintering techniques. Appropriate amounts of Sn and Te were sealed into an evacuated fused quartz tube and melted at 900° C. On removal from the tube the ingot was crushed and ground. The powder was then compacted in a split tungsten carbide die into cylinders typically of 3/4 in. diameter by 1 in. length. Each cylinder was sealed into an evacuated quartz tube and sintered at 500° C for a week. Silver- and Mn-doped samples were prepared by melting the required amount of material in vacuum and electromagnetically stirring during melting and solidification. This technique was found to prevent oxidation of Mn during preparation (3). It also yielded samples which were very uniform and homogeneous in phase, as indicated by X-ray lattice parameter studies. A small Hall sample of size 1/8" x 1/2" was cut from each ingot to determine the low field Hall constant, R, at 77° K. The range of $n_H = 1/Re$ was from 2×10^{20} to 6.5×10^{21} cm^{-3}.

Most heat capacity measurements were performed in He^3 and adiabatic demagnetisation cryostats (4) covering the temperature span from 0.06 to 20° K. For temperatures from 1.8° to 30° K, some measurements were made in a modified pulse type calorimeter(5). The accuracy of the measurements was checked by measuring the heat capacity of pure copper. The electronic and lattice terms were both within 0.5% of previously determined values (6).

Results and Discussion

1. Non-magnetic Doping

Our heat capacity data for self-doped and Ag-doped samples can be fitted by the normal expression $C = \gamma T + \alpha T^3$, where γT and αT^3 are the electronic and lattice contribution, respectively. The Debye temperature θ_D has an average value of 147 K and does not vary systematically with dopant or carrier concentration.

In Fig. 1, the electronic heat capacity coefficient is plotted against the inverse Hall coefficient $1/Re = n_H$. A simple, free carrier model predicts that γ should be proportional to $n^{1/3}$. In SnTe this appears to be the case for $n > 4 \times 10^{20}$ cm^{-3}, but a definite departure from this behavior occurs at lower carrier densities. The occurrence of γ values substantially below the $n^{1/3}$ line for $n < 4 \times 10^{20}$ is well outside the limits of experimental error. For $n_H < 4 \times 10^{20}$ cm^{-3}, the thermal effective mass is $m_d = 2.1$, and for $n_H > 2.3 \times 10^{20}$ cm^{-3}, $m_d = 1.2$.

Of the valence band models which have been proposed for SnTe (7), those that include two or more sets of degenerate bands are consistent with these results. The shape of γ vs $1/Re$ is qualitatively explained by the occupation of a second set of bands above $n_H \sim 4 \times 10^{20}$ cm^{-3}. A more quantitative analysis of the proposed models and the contributions of different bands to γ would require additional electrical measurements on the present samples to obtain the relative populations from $1/Re$. In some of the models of SnTe the upper valence band extrema are placed at the L point of the zone and have a fourfold degeneracy. The resulting spherical

band mass for this type of band is 0.25 where the mass enhancement factor $1 + \lambda$ is obtained from previous superconducting transition temperature measurements. This band mass is not grossly inconsistent with the electrical susceptibility mass determined from optical measurements (8). If the second set of bands starts to fill at $n_H = 4 \times 10^{20}$ cm^{-3}, a band mass of 0.25 gives a 0.3 ev separation of the two bands. This value agrees with those given by many of the models.

2. Magnetic Doping

It is known (3) that Mn goes substitutionally into the SnTe matrix. Magnetic measurements indicate that the Curie temperature of $Sn_{.97-y}Mn_yTe$ varies linearly with y. In order to determine the effect of magnetic ordering on the heat capacity, samples with $0 < y < 0.10$ were measured.

It seems reasonable to approximate the total heat capacity of the alloys, C_{alloy}, by the sum of a magnetic term C_M and a normal heat capacity C of $Sn_{.97}Te$, as defined earlier. This allows us to separate C_M from C_{alloy}. In Fig. 2 we plot C_M/T vs T for four representative samples. The heat capacity anomaly associated with the Mn spins is shifted to lower temperatures with decreasing y, as expected.

For $y \leq 0.05$, for which C_M/T vanished at high temperature, the extra entropy due to Mn ions was calculated. It was found to be approximately proportional to y, and consistent with $R\ln(2S + 1)$ per mole Mn, where $S = 5/2$ is the Mn ion spin obtained from the magnetic susceptibility measurements (3). For $y = 0.01$, the peak of the specific heat curve is

unusually sharp for a disordered alloy (10).

The nonvanishing C_M/T term for higher manganese contents appears to be essentially constant up to at least 30° K. This effect may be associated with localized enhancement of the density of states, clustering of ferromagnetic impurities, or inadequacy of the approximation that the background heat capacity is independent of y. (No indication of clustering was obtained from susceptibility data.)

The heat capacity of one sample, $Sn_{.97}Mn_{.01}Te$, was measured in various applied magnetic fields ranging up to 30 kOe. The excess heat capacity of $Sn_{.97}Mn_{.01}Te$ relative to $Sn_{.97}Te$ is shown in Fig. 3. In general appearance, the observed heat capacity curves closely resemble Schottky curves. The best fit to the data is for spin 5/2, as shown in Fig. 3.

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FIGURE CAPTIONS

Figure 1 Dependence of γ on carrier concentration of $Sn_{1-x}Te$ and $Sn_{1-x}Ag_yTe$.

Figure 2 Magnetic heat capacity C_M of $Sn_{.97-y}Mn_yTe$ for various y values.

Figure 3 Magnetic heat capacity C_M of y = 0.01 Mn sample in various external fields. Solid lines are theoretical 5/2 Schottky curves.

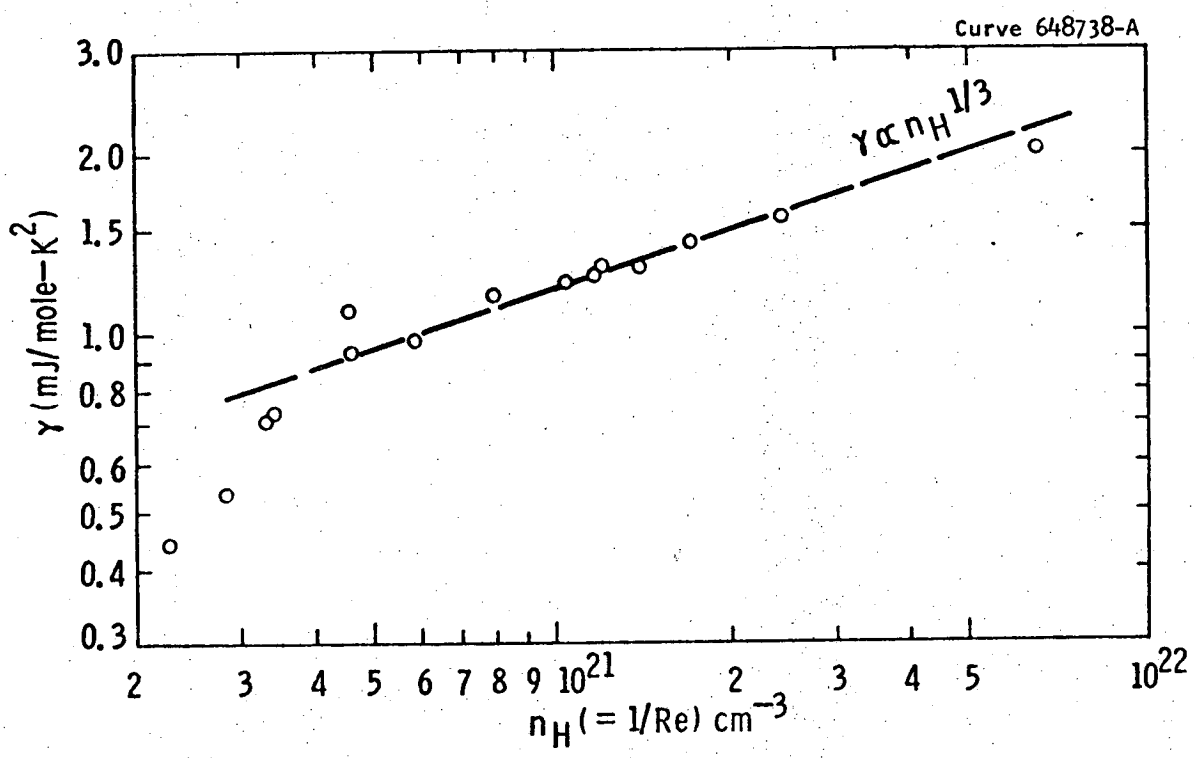
Curve 648738-A
3.0
2.0
1.5
1.0
0.8
0.6
0.5
0.4
0.3
γ (mJ/mole-K²)
γ ∝ n_H^1/3
2
3
4
5
6
7
8
9
10^21
2
3
4
5
10^22
n_H (= 1/Re) cm^-3

Fig. 1

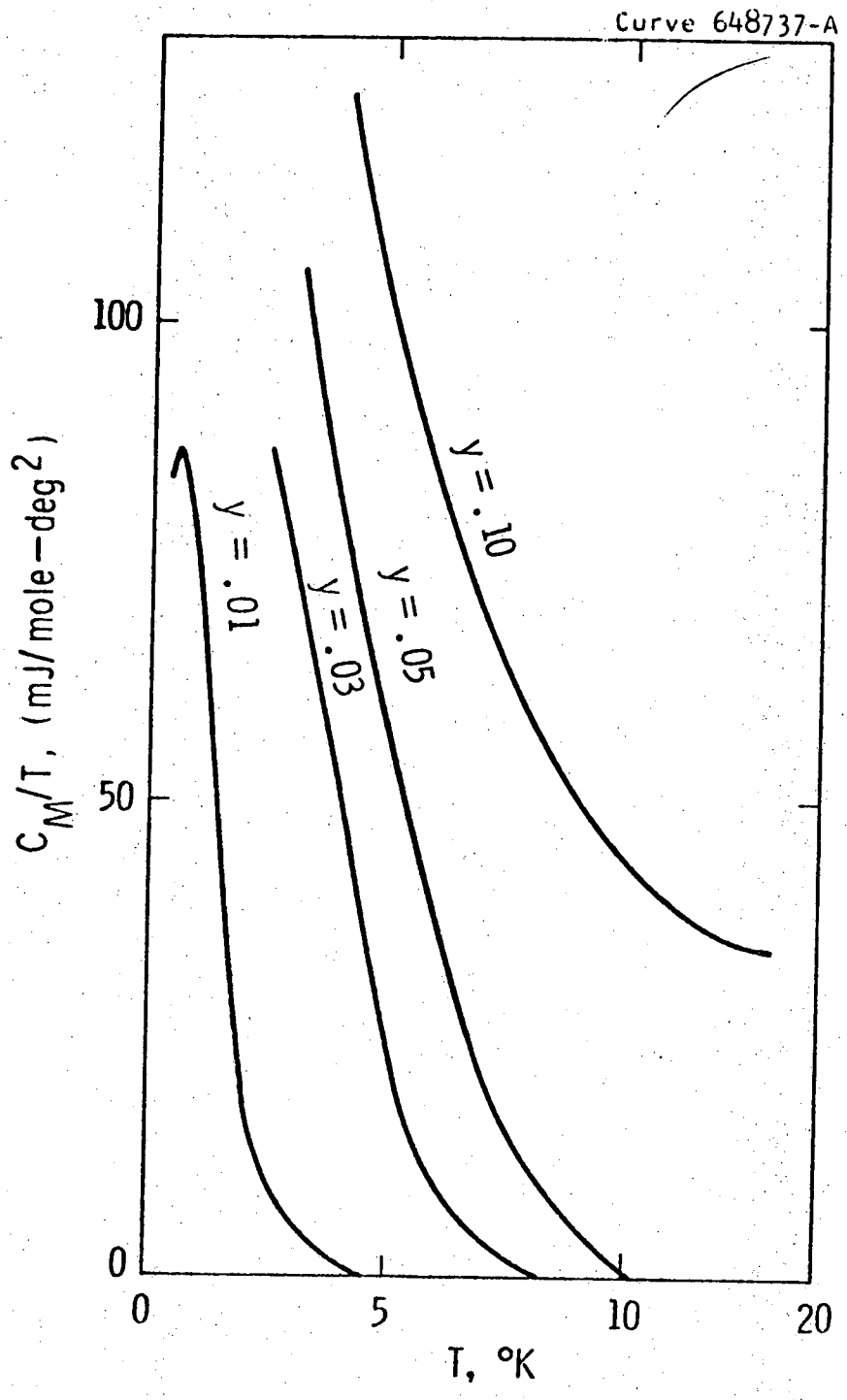
Curve 648737-A
100
50
0
0
5
10
20
C_M/T, (mJ/mole−deg^2)
T, °K
y = .01
y = .03
y = .05
y = .10

Fig. 2

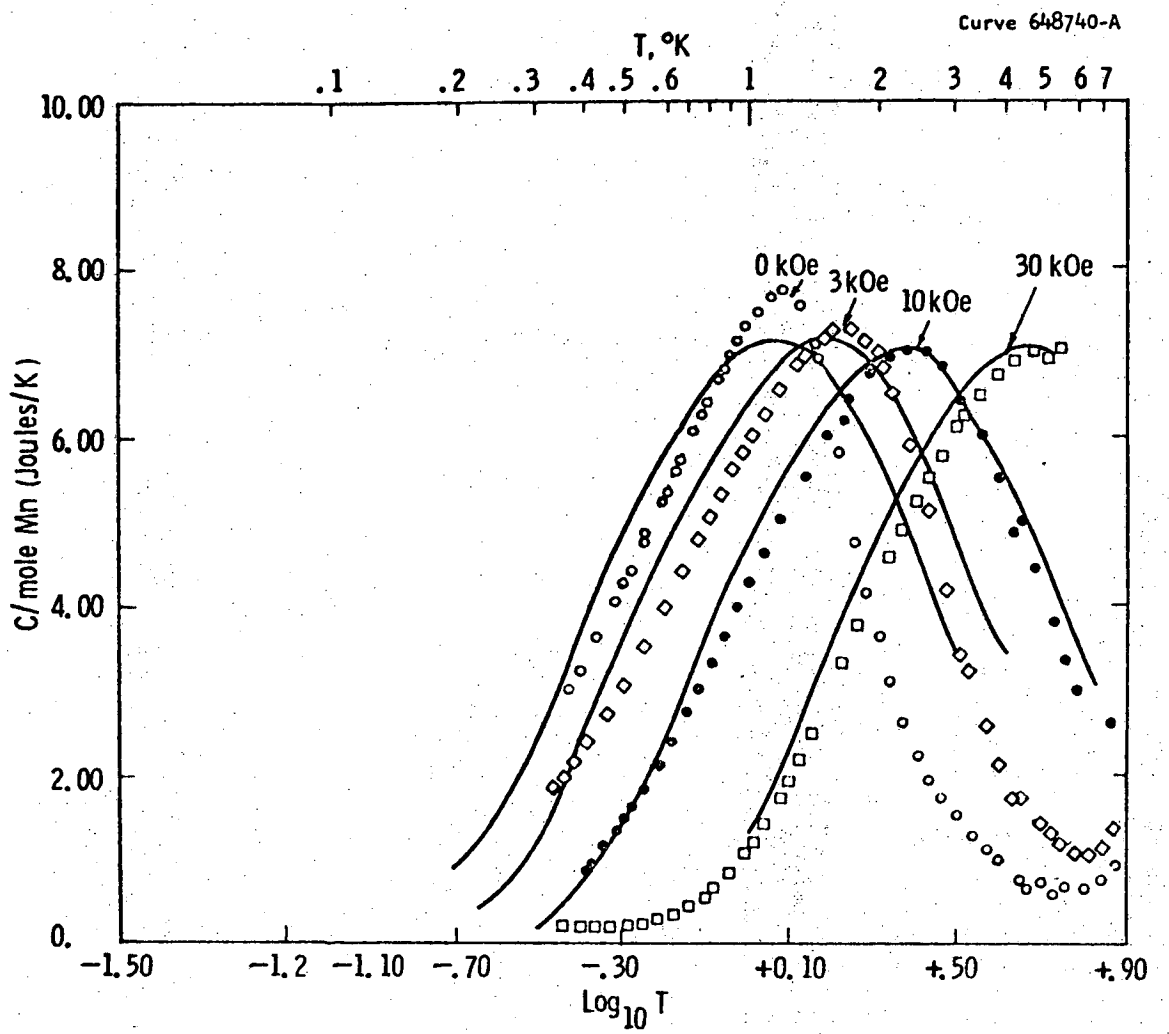
Curve 648740-A
T, °K
.1
.2
.3
.4
.5
.6
1
2
3
4
5
6
7
10.00
8.00
6.00
4.00
2.00
0.
C/mole Mn (Joules/K)
0 kOe
3kOe
10kOe
30 kOe
−1.50
−1.2
−1.10
−.70
−.30
+0.10
+.50
+.90
Log10 T

Fig. 3

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