

Presented at the 13th Int. Conf. on
Low Temperature Physics,
Boulder, Colorado, Aug. 21-25, 1972

RECEIVED
LAWRENCE
RADIATION LABORATORY

LBL-1137

NOV 20 1972

LIBRARY AND
DOCUMENTS SECTION

SPECIFIC HEAT OF SnTe BETWEEN 0.06 K
AND 30 K UNDER STRONG MAGNETIC FIELD

M. P. Mathur, M. Ashkin, J. K. Hulm,
C. K. Jones, M. M. Conway, N. E. Phillips,
H. E. Simon, and B. B. Triplett

August 1972

AEC Contract No. W-7405-eng-48

For Reference

Not to be taken from this room



LBL-1137

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

SPECIFIC HEAT OF SnTe BETWEEN 0.06 K AND 30 K
UNDER STRONG MAGNETIC FIELD*

M.P. Mathur, M. Ashkin, J.K. Hulm and C.K. Jones
Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

and

M.M. Conway, N.E. Phillips, H. E. Simont† and B. B. Triplett‡
Inorganic Materials Research Division
of the Lawrence Berkeley Laboratory and the
Department of Chemistry, University of California,
Berkeley, California 94720

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 $1/8'' \times 1/2''$ was cut from each ingot to determine the low field Hall constant, R , at 77°K . The range of $n_{\text{H}} = 1/R_e$ was from 2×10^{20} to $6.5 \times 10^{21} \text{ cm}^{-3}$.

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 $1/R_H = n_H$. A simple, free carrier model predicts that γ should be proportional to $n^{1/3}$. In SnTe this appears to be the case for $n > 4 \times 10^{20} \text{ cm}^{-3}$, 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 $n_H < 4 \times 10^{20} \text{ cm}^{-3}$, the thermal effective mass is $m_d = 2.1$, and for $n_H > 2.3 \times 10^{20} \text{ cm}^{-3}$, $m_d = 1.2$.

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 $1/R_H$ is qualitatively explained by the occupation of a second set of bands above $n_H \sim 4 \times 10^{20} \text{ cm}^{-3}$. 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 $1/R_H$. 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 $n_H = 4 \times 10^{20} \text{ cm}^{-3}$, 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 $\text{Sn}_{.97-y}\text{Mn}_y\text{Te}$ 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 $\text{Sn}_{.97}\text{Te}$, 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, $\text{Sn}_{.97}\text{Mn}_{.01}\text{Te}$, was measured in various applied magnetic fields ranging up to 30 kOe. The excess heat capacity of $\text{Sn}_{.97}\text{Mn}_{.01}\text{Te}$ relative to $\text{Sn}_{.97}\text{Te}$ 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.

* Work at Westinghouse supported in part by the U.S. Air Force Office of Scientific Research under contract # F44620-72-C-0035. Work at Berkeley supported by U.S. Atomic Energy Commission.

† Present address Department of Chemistry, University of California, La Jolla, California 92037.

‡ Present address Department of Physics, Stanford University, Stanford, California 94305.

REFERENCES

1. J. K. Hulm, C. K. Jones, D. W. Deis, H. A. Fairbank and P. A. Lawless, Phys. Rev. 169, #2, 388 (1968).
2. J. K. Hulm, M. Ashkin, D. W. Deis and C. K. Jones, Prog. Low Temp. Phys. Vol. VI, Ed. C. J. Gorter, North-Holland Publishing Co.
3. M. P. Mathur, D. W. Deis, C. K. Jones and W. J. Carr, Jr., Journ. of Appl. Physics 41, #3, 1005 (1970).
4. B. B. Triplett, Ph. D. Thesis, University of California, Berkeley, UCRL-19672, Sept. 1970, unpublished.
5. F. J. Morin and J. P. Maita, Phys. Rev. 129, 1115 (1963).
6. D. W. Osborne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instru. 38, 159 (1967).
7. H. Kochler, Z. Angew, Phys. 23, 270 (1967).
8. R. Tsu, W. E. Howard and L. Esaki, Phys. Rev. 172, 779 (1968).
9. R. F. Bis, J. R. Dixon, Phys. Rev. B 2, 1004 (1970).
10. W. Marshall, Phys. Rev. 118, 1519 (1960).

FIGURE CAPTIONS

- Figure 1 Dependence of γ on carrier concentration of Sn_{1-x}Te and $\text{Sn}_{1-x}\text{Ag}_y\text{Te}$.
- Figure 2 Magnetic heat capacity C_M of $\text{Sn}_{.97-y}\text{Mn}_y\text{Te}$ 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.

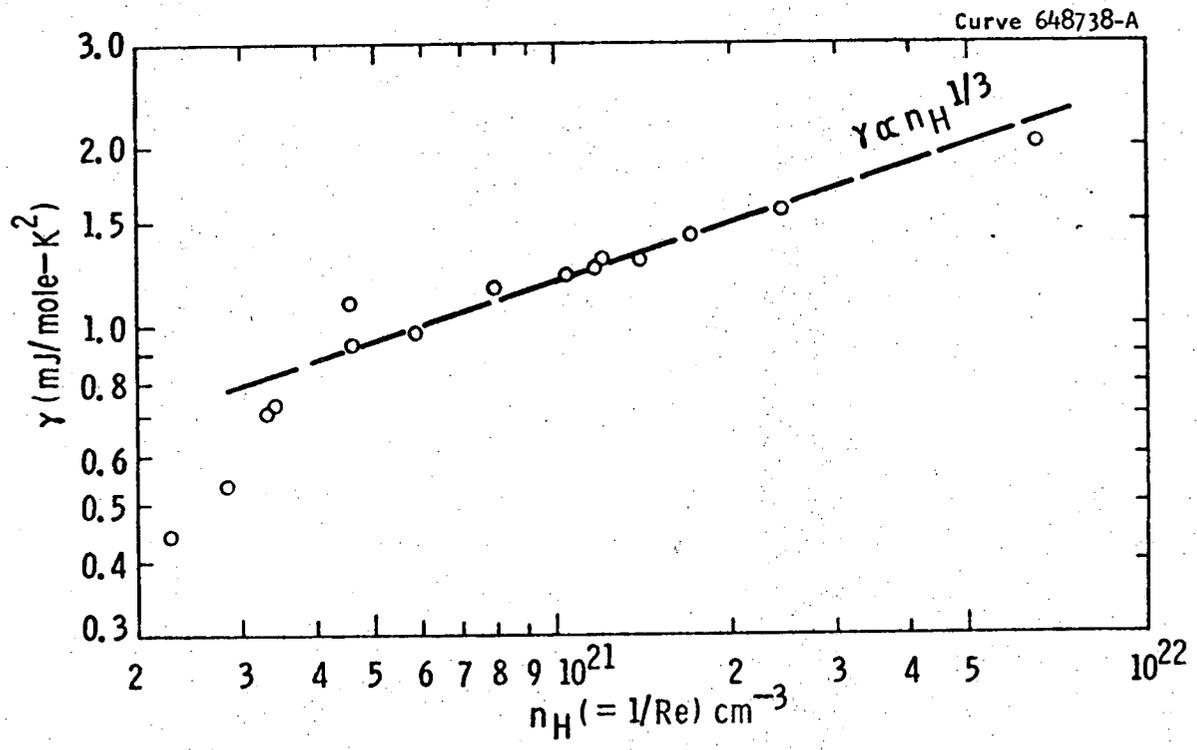


Fig. 1

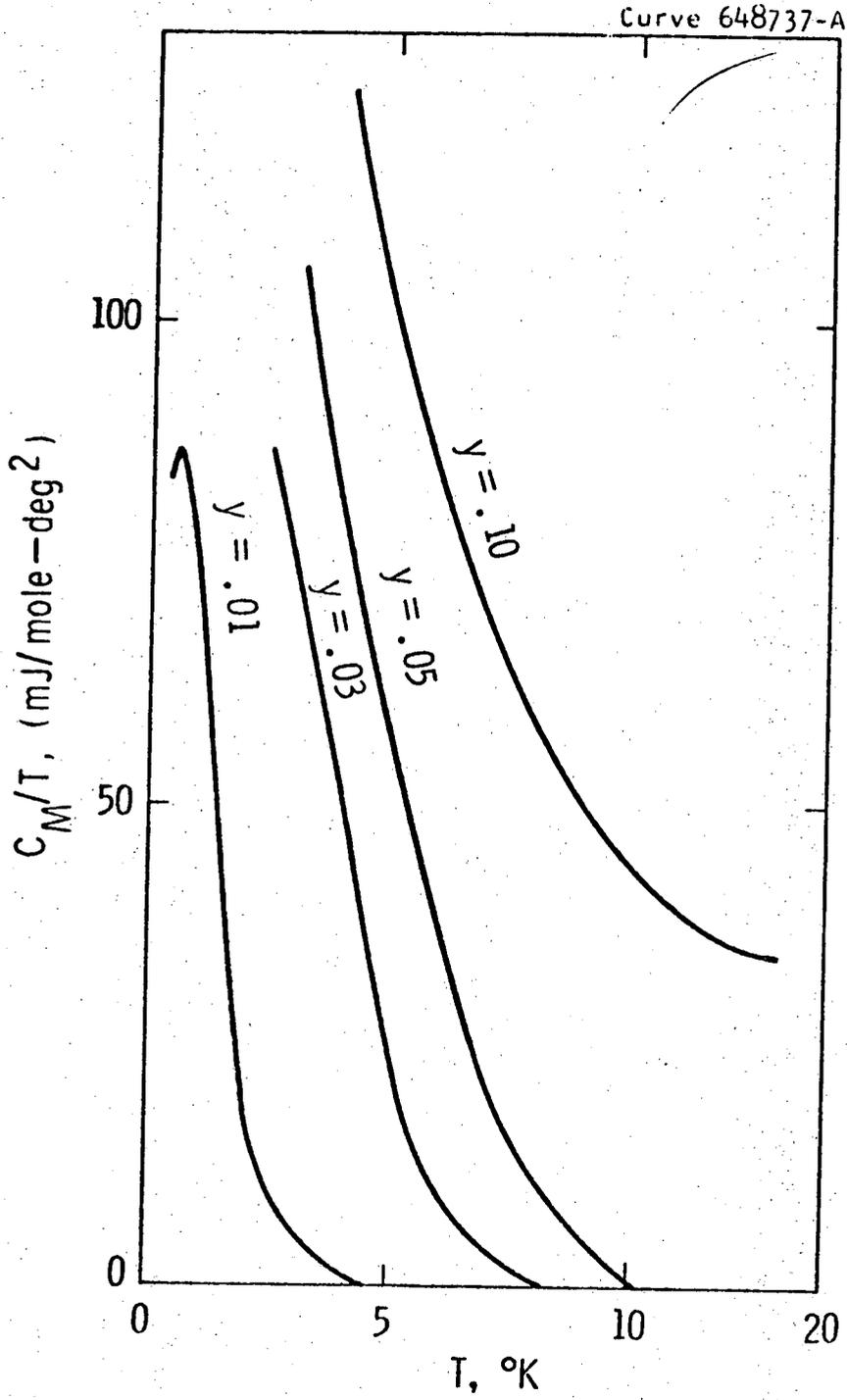


Fig. 2

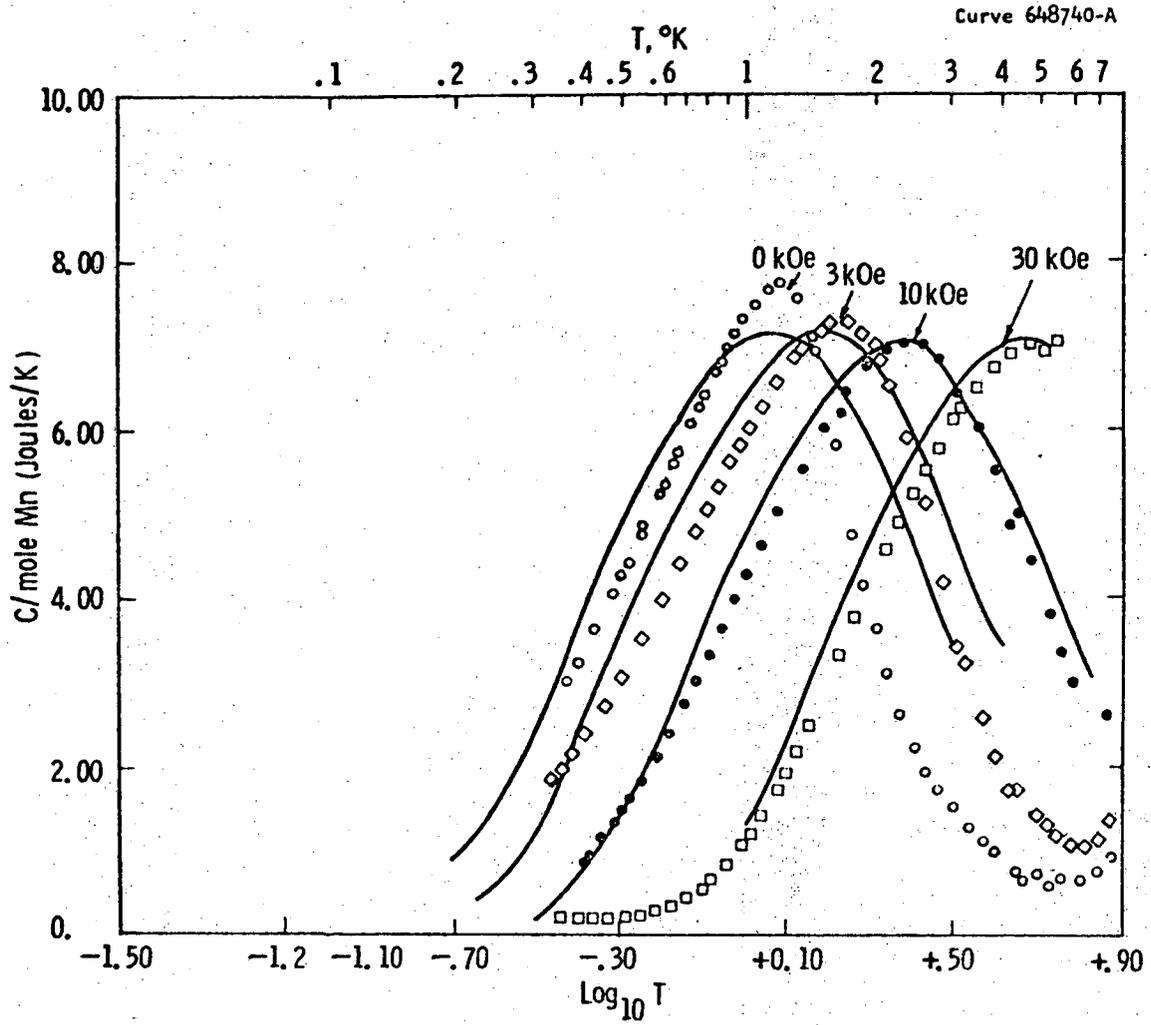


Fig. 3

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720