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July 1964

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According to M. L. Cohen's¹ theoretical predictions, certain many-valley semiconductors and semimetals may be superconductors at experimentally accessible temperatures. Hein et al.² have examined germanium telluride containing a large number of carriers. They find that it does indeed show those changes in magnetic susceptibility with temperature to be expected of a superconductor. However, susceptibility (and resistivity) measurements do not exclude the possibility of the superconductivity being confined to unrepresentative regions of the sample (Hein et al.). The heat capacity measurements presented here show that at least the major part of the germanium telluride sample was superconducting, and hence that the superconductivity observed by Hein et al. is a true bulk effect.

A germanium telluride sample of the type used by Hein et al. was kindly supplied to me by Dr. J. K. Hulm. It was a specially prepared large (one gram-mole) cylinder of nominal composition $\text{Ge}_{.950}\text{Te}$, annealed for ten days at 485°C . Attached to the sample were a carbon (painted colloidal graphite) resistance thermometer, manganin heater, copper, varnish, and a negligible amount (< 0.001 mole) of lead in a superconducting heat switch. The apparatus was that described by O'Neal and Phillips³. For each series of heat capacity measurements, the sample

was cooled (by a demagnetised salt) to below 0.05°K in a field of less than 0.1 gauss. Measurements were then made covering the range from 0.1° to 1.1°K . The carbon thermometer was calibrated by the susceptibility of a cerium magnesium nitrate sphere, which was in turn calibrated against the 1958 helium vapour pressure temperature scale.

The observed specific heat (C) between $T = 0.3^{\circ}\text{K}$ and 0.9°K is a good fit to $C = \gamma T + aT^3$. Below 0.3°K a well-defined specific heat maximum is observed (Fig. 1). The position (0.17° - 0.27°K) of the high-temperature side of the maximum is at about the same temperature as the susceptibility change reported by Hein et al. The broadening of the maximum is probably due to sample inhomogeneity: it is difficult to make a large sample of high carrier concentration. A field of 500 gauss caused the maximum to disappear. The points below 0.3°K then agree well with an extrapolation of the higher temperature ones when no field was applied. Entropy considerations show that at 0°K any linear term in the specific heat, with no applied field, is less than half its value in a field of 500 gauss. Thus the existence of bulk superconductivity in germanium telluride may be considered established.

From the full set of measurements to above 0.9°K , the Debye characteristic temperature $\theta = 166 \pm 3^{\circ}\text{K}$, and the electronic specific heat coefficient $\gamma = 1.32 \pm 0.02 \text{ mJ mole}^{-1}(\text{K})^{-2}$. It is possible to estimate from γ the number of contributing maxima in momentum space following, for example, Keesom and Seidel⁴. It is interesting to note that the γ reported here, together with reasonable values for the effective mass, indicates an effective number of maxima greater than one and probably equal to three, which is in agreement with the energy band structure scheme for germanium telluride of M. H. Cohen et al.⁵ It is hoped to do

further measurements on samples of different carrier concentrations to aid our understanding of the band structure and superconductivity mechanism.

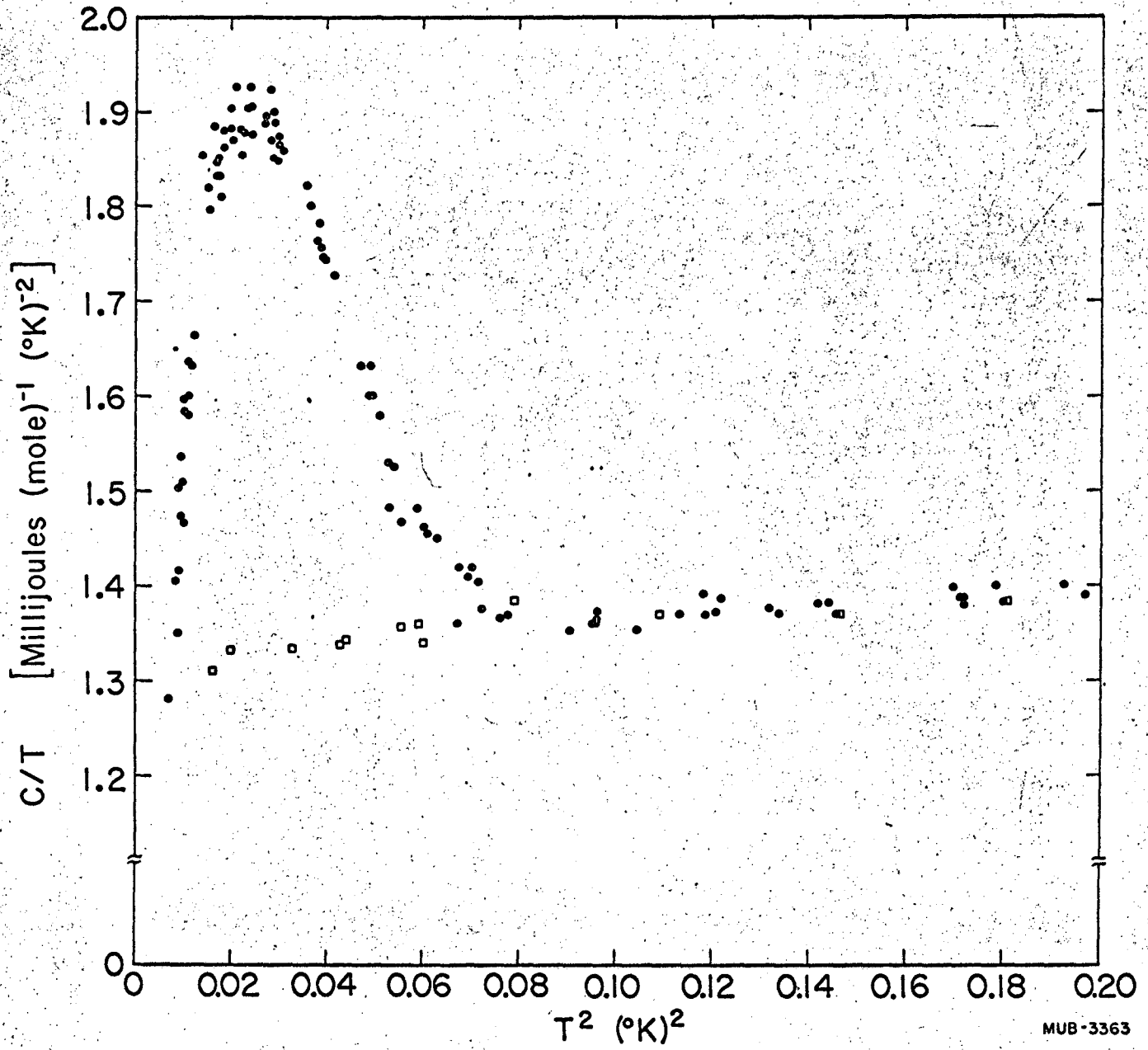
I am most grateful to Drs. John K. Hulm and R. Mazelsky of the Westinghouse Research Laboratories, Pittsburgh, for providing the sample, and to Dr. Hulm for several helpful discussions. Also I wish to thank my colleagues, particularly Dr. M. H. E. R. Lambert, for advice and encouragement, and Professor N. E. Phillips for the use of his apparatus and the facilities of his laboratory.

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FIGURE CAPTIONS

Fig. 1. Heat capacity of germanium telluride at low temperatures, with no field (⊙) and with 500 gauss (□) applied.



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Fig. 1

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