

FIG. 2. Photon emission from electron-bombarded Mg foil (spectrum uncorrected for spectrometer response).

was inserted into the light path. The peak at 815 Å disappeared when the filter was inserted. As a further test, experiments with electron-bombarded Ag and Au foils showed no such peak in this region. Foils of Mg were also bombarded yielding a broad peak at 1400 Å and a sharp peak

at 1800 Å (Fig. 2) in good agreement with characteristic energy loss experiments. Whether the optical emission at 1800 Å corresponds to the 7.0-eV surface plasmon loss remains to be seen. The improved resolution obtainable by measuring photon energies instead of electron energies makes possible detailed investigations of characteristic energy losses heretofore limited by the difficulty in making accurate electron energy loss measurements.

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¹R. A. Ferrell, Phys. Rev. **111**, 1214 (1958).

²W. Steinmann, Phys. Rev. Letters **5**, 470 (1960); R. W. Brown, P. Wessel, and E. P. Trounson, Phys. Rev. Letters **5**, 472 (1960); H. Boersch, C. Radeloff, and G. Sauerbrey, Phys. Rev. Letters **7**, 52 (1961).

³A. L. Frank, E. T. Arakawa, and R. D. Birkhoff, Phys. Rev. **126**, 1947 (1962).

⁴H. Ehrenreich and H. R. Philipp, Phys. Rev. **128**, 1622 (1962).

⁵C. J. Powell and J. B. Swan, Phys. Rev. **118**, 640 (1960).

⁶W. R. Hunter, J. Opt. Soc. Am. **54**, 208 (1964).

⁷R. H. Ritchie and H. B. Eldridge, Phys. Rev. **126**, 1935 (1962).

SUPERCONDUCTIVITY IN GERMANIUM TELLURIDE

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Theoretical calculations by Cohen¹ have indicated that highly doped, many-valleyed semiconductors and semimetals might become superconducting at temperatures around 0.1°K. We report here some results on germanium telluride, a material which at normal temperatures behaves like a *p*-type semiconductor² with moderate mobility ($\mu \sim 100$) and high effective mass ($m^*/m_0 \sim 1$). Due to the large number of carriers, $\eta \sim 0.9 \times 10^{21}$, the forbidden gap has never been accurately

determined. At a temperature $\sim 50^\circ\text{C}$ below the melting point (723°C), the resistivity starts to decrease with increasing temperature indicating a gap of very roughly 1/2 to 1 eV. Above about 400°C the crystal structure is cubic and at lower temperatures it is rhombohedral. The rhombohedral angle decreases from 90° above the transition to $\sim 88\frac{1}{2}^\circ$ at room temperature and is essentially constant at lower temperatures.

Our measurements show that this material be-

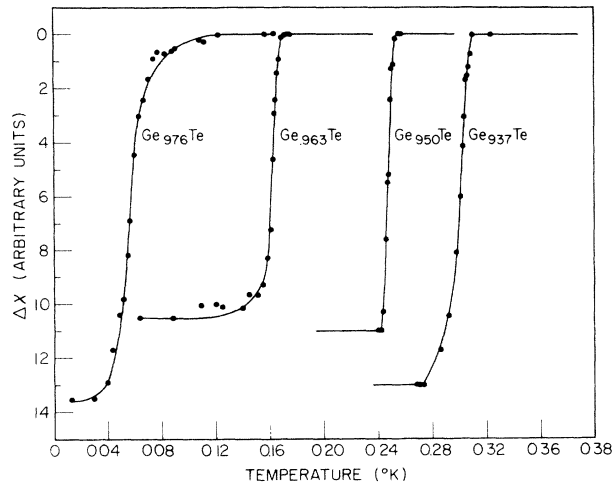


FIG. 1. Changes in the initial susceptibility ($\Delta\chi$) of the samples as a function of the temperature. The large differences in the values of the superconducting levels in this figure are due to differences in the sensitivity of the mutual inductance circuits employed.

comes superconducting in the predicted temperature range and that the transition temperature is a function of the composition. In Fig. 1 are plotted the transition curves for four pressed and sintered samples of germanium telluride with the stated nominal composition. Similar results have also been obtained on melted specimens. Cohen has emphasized that if superconductivity does occur among semiconductors and semimetals, the transition temperature should be a function of the number of carriers present in the sample. Figure 2 is a plot of the transition temperatures as a function of the number of carriers. The carrier concentration was calculated from the low-field Hall coefficient measured at 77°K using the relation $R = 1/\eta e$. The carrier concentration obtained in this fashion for the sample of composition $\text{Ge}_{0.976}\text{Te}$ is in good agreement with that calculated assuming two holes per germanium vacancy. For the more heavily doped samples the measured concentration is less than that calculated from the composition, probably indicating that excess tellurium did not completely dissolve. These data strongly suggest that some correlation between these quantities does exist; however, the paucity of the present data precludes any firm conclusion about the exact nature of this correlation. The apparent cutoff in superconductivity when the number of carriers falls below 8.5×10^{20} is in keeping with our failure to observe a transition in a sample with the nominal composition

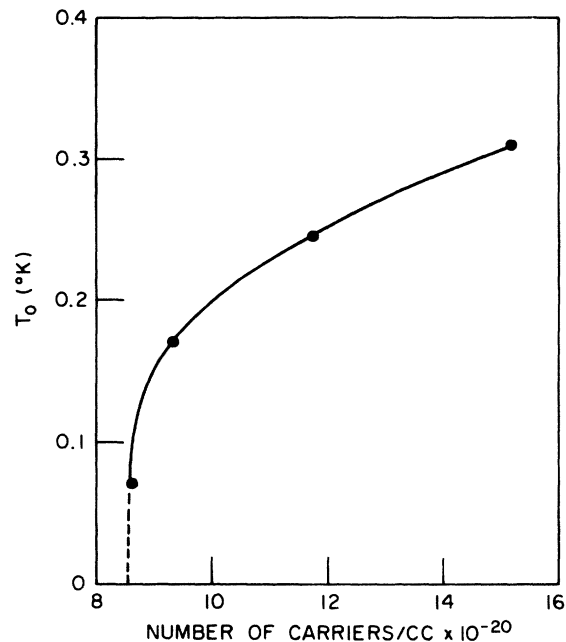


FIG. 2. The zero magnetic field transition temperatures, T_0 , as a function of the carrier concentration for the GeTe samples of Fig. 1. The carrier concentrations were deduced from Hall voltage measurements.

$\text{Ge}_{1.006}\text{Te}$ in which the concentration of carriers was 7.5×10^{20} per cc. It is interesting to point out that this result is consistent with Chapnik's empirical predictions.³

Temperatures below 1°K were produced by the magnetic cooling method utilizing potassium chrome alum as the cooling agent. Superconductivity was detected by means of a dc mutual inductance method.⁴ In the present work the samples were shielded from external magnetic fields by means of a Mu-metal case. Since the measuring field was 0.2 oersted, the observed quantity is essentially the temperature dependence of the initial slope of the magnetization curves of the samples.

When we first observed superconductivity in an ingot of composition ($\text{Ge}_{0.976}\text{Te}$), we were concerned about the possibility that we were observing the effects of some superconducting impurity. Although the low value of the transition temperature (0.08°K) made such an explanation somewhat remote, we nevertheless ran a controlled experiment, as follows: Samples of the original Ge and Te as well as the resulting $\text{Ge}_{0.976}\text{Te}$ compound were cooled to temperatures as low as 0.04°K and a superconducting transition was observed only for the compound. Thus we rule out the ef-

fects of any foreign superconducting impurity. We have also detected superconductivity in powdered specimens, ruling out the possibility of a superconducting second phase. We have observed transitions in the presence of applied magnetic fields. Such transitions display the hysteretic behavior typical of most superconducting alloys and compounds.

Comparison of the zero-field transition observed for $\text{Ge}_{0.976}\text{Te}$ with that obtained for a geometrically identical sample of Sn leads one to the conclusion that the GeTe sample exhibited complete diamagnetic shielding. The experimental accuracy on this point is approximately 5%. The observation of complete shielding constitutes merely a necessary and not a sufficient observation from which one can conclude that the entire volume of

the sample has entered the superconducting state. Keeping in mind this limitation of the data, we feel that the superconductivity of GeTe is as firmly established as is that of most other superconducting alloys and compounds.

¹M. L. Cohen, Rev. Mod. Phys. (to be published); Phys. Rev. (to be published).

²R. C. Miller, Thermoelectricity: Science and Engineering, edited by R. R. Heikes and R. W. Ure, Jr. (Interscience Publishers, New York, 1961), Sec. 13.6, pp. 434-442.

³I. M. Chapnik, Dokl. Akad. Nauk. SSSR 141, 70 (1961) [translation: Soviet Phys. "Doklady" 6, 988 (1962)].

⁴R. A. Hein and J. W. Gibson, Phys. Rev. 131, 1105 (1963).

SILSBEE-LIMIT CRITICAL CURRENTS IN A 1700 Å FILM OF TIN

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Reported in this Letter are some new pulse measurements of critical currents obtained from an evaporated film of tin whose thickness was 1700 Å. The current pulse amplitudes required to induce 90% of the normal film resistance within the observed response time of the equipment are in good agreement, over a wide temperature range, with the Silsbee hypothesis for bulk tin, if latent heat effects are taken into account. Film imperfections, coupled with Joule heating in pulse measurements, have apparently limited previous measurements¹⁻⁸ to values substantially less than the Silsbee limit even when the films were sufficiently thick so that the Silsbee value should have been applicable.⁹ Joule heating effects have been reduced in the results reported herein by using current pulses less than 10^{-9} sec in duration, compared to the $\geq 10^{-8}$ sec used earlier.^{2,6,7}

Only a brief description of the experimental arrangement will be given here. The film of tin was evaporated onto a rapidly rotating (1800 rpm) hollow glass tube at about 1000 Å/sec in a vacuum of about 5×10^{-6} Torr. The thickness was determined from the temperature-dependent part of the resistance.¹⁰ The superconducting transition temperature and transition width were 3.76°K and 0.017°K and were obtained with a measuring current of 10^{-2} A. The residual resistance was 0.029 of the room temperature resistance. Sondheimer's

results¹¹ indicate that this residual resistance arises predominantly from electronic surface scattering (if the surface scattering is assumed to be diffuse). Consequently, this film appears to be relatively pure.

Current pulses with a measured rise time of $\leq 2 \times 10^{-10}$ sec were generated by conventional coaxial line discharging techniques¹² employing a coaxial mercury relay. These current pulses passed through the thin film sample which was in the form of a hollow cylinder, 0.0283 inch in diameter and about 3/8 inch in length. The film sample constituted the end section of the outer conductor of the coaxial line in which the current pulse was generated. The center and outer conductors of this line were shorted together immediately beyond the film sample. A second coaxial line, concentric with the first and using the film sample as a portion of its center conductor, allowed the signal induced by a current pulse flowing through the resistive film sample to propagate out of the helium bath and into a sampling oscilloscope (response time $\leq 10^{-10}$ sec). This detection arrangement eliminates, at least, in principle, inductive coupling between the two coaxial lines and also can be built with a sufficiently wide-band frequency response to be commensurate with the sampling oscilloscope. An additional advantage of this arrangement is its