J. Phys. Chem. Solids Pergamon Press 1958. Vol. 7. pp. 228–235.

PREPARATION AND ELECTRICAL PROPERTIES OF MERCURY TELLURIDE*

T. C. HARMAN, M. J. LOGAN and H. L. GOERING

Battelle Memorial Institute

(*Received* 14 *May* 1958)

Abstract—Mercury telluride has been prepared by direct reaction of mercury vapor with liquid tellurium. The compound was zone melted and annealed in mercury vapor under various pressures of mercury. It was found that the composition near stoichiometry could be altered by the anneal. Hall coefficient and resistivity were measured as a function of temperature. Analysis of the results gave 0·02 eV for the energy gap at 0°K and a hole to electron mobility ratio of 0·01. The Hall mobility was 17,000 cm^2/Vsec at 300°K and 25,000 cm^2/Vsec at 143°K.

INTRODUCTION

FOR the past several years, there has been considerable interest in semiconducting compounds. In this paper, results of studies on the preparation and electrical properties of mercury telluride are given. The electrical properties were markedly changed by annealing in mercury vapor. The preparation, zone melting, annealing, and electrical properties of HgTe are described.

PREPARATION OF MERCURY TELLURIDE

Mercury with an estimated purity of 99·99$^+$ per cent and tellurium which had been sublimed twice in a stream of hydrogen at approximately 800°C were used to prepare the compound. The purification technique for tellurium has been described previously.(1) The elements were placed in a Vycor boat (1·9 cm × 20 cm) and sealed in an evacuated quartz tube (2·2 cm × 56 cm).

The compound was prepared by the two-zone-furnace technique which provided a uniform high-temperature zone for melting and casting the ingot, and a low-temperature zone, which could be varied independently of the other zone, for controlling the vapor pressure of mercury in the system. The material was maintained at the melting point (~ 670°C) for a period of 4 hr or longer; the vapor pressure of mercury was maintained at about 15 atm. In cooling the system, the mercury vapor pressure was always kept equal to or greater than the upper limit of the dissociation pressure of the compound. The upper limit of this pressure at temperatures below the melting point was assumed to be half the vapor pressure of pure mercury at the same temperature.

Under a mercury vapor pressure of about 15 atmospheres, the melting point of the compound was established to be 670±5°C, which is the value quoted in the literature.(2)

ZONE MELTING OF MERCURY TELLURIDE

The early zone-melting experiments were carried out under 5 and 10 atm of mercury and resulted in extremely polycrystalline HgTe. From zone-melting work with other compounds, it is known that extremely polycrystalline material usually results if the ambient pressure of the volatile constituent is maintained considerably below the dissociation pressure of the compound. (The dissociation pressure may be thought of as the vapor pressure of the volatile constituent in equilibrium with the compound at a specific temperature.) Additional experiments were carried out under a mercury pressure of 15 atm. It was found that if the ingot temperature is too low, the carefully crystallized solid melts because of alloying, and the subsequent rapid nondirectional freeze results in extremely polycrystalline material. This

---

* This research was supported by Engineer Research and Development Laboratory, Fort Belvoir, under Contract No. DA–44–009–Eng–3199.

alloying phenomena was also observed in annealing experiments. It is concluded that to zone melt HgTe successfully, there must be three carefully controlled temperature zones which have the following limitations. One temperature zone, T_1, is for the molten zone (see Fig. 2) which is, of course, at the melting point of the compound. A second zone, T_2, is for the solidified ingot and cannot be too high in temperature or too low in temperature. A temperature appreciably higher than the allowable range for T_2 would prevent formation of a sufficient temperature gradient for recrystallization, while a temperature appreciably lower would favor alloying and consequent melting of the compound. The third temperature zone, T_3, controls the mercury pressure. It can be neither too high in temperature because of the possibility of alloying, nor too low in temperature because of resulting loss of mercury from the liquid zone due to dissociation of the compound. After several experiments, it was found that satisfactory conditions for zone melting HgTe are achieved with the ingot temperature at 620°C (approximately 50°C below the melting point of the compound) and the temperature controlling the mercury pressure at about 560°C, corresponding to a mercury pressure of approximately 15 atm. As shown in Fig. 1, the zone-melting apparatus for HgTe is similar to the

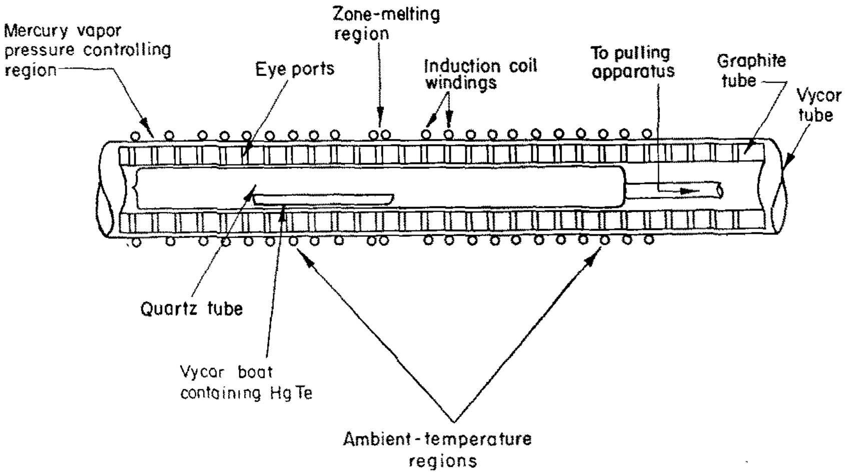

FIG. 1. Apparatus for zone melting.

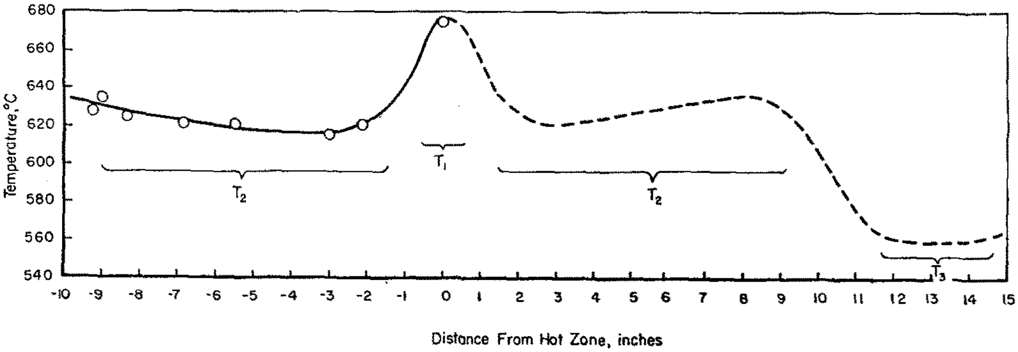

FIG. 2. Temperature distribution along graphite tube used for zone melting HgTe.

one described in reference (1). However, the number of eye ports was increased to allow visual observation of the entire tube. Thus, alloying and condensation of mercury could be observed directly. The temperature distribution along the graphite tube in Fig. 1 is shown in Fig. 2.

The temperature minima in zones T_2 and T_3 must not deviate more than 10°C from the values shown in Fig. 2. Zone-melt passes at a recrystallization velocity of 1·2 cm/hr were carried out. Specimens removed from the ingots for annealing experiments and investigation of electrical properties possessed several crystallites and were believed to be of sufficient quality to obtain accurate information on energy gap and mobilities of the compound. It is concluded that nearly single-crystal specimens of HgTe can be cut from ingots of HgTe zone melted under the temperature conditions shown in Fig. 2 and at recrystallization rates of about 1·0 cm/hr. The effectiveness of removing foreign impurities from HgTe by the zone-melt technique has been discussed by Black *et al.*(3)

ANNEALING OF HgTe IN MERCURY VAPOR

Studies(4) on CdTe have shown that annealing the compound in cadmium vapor at pressures above the dissociation pressure of the compound results in *n*-type CdTe, while annealing the compound in cadmium vapor at pressures below the dissociation pressure of the compound results in *p*-type CdTe. It was anticipated that the same techniques could be used for altering the composition near stoichiometry of HgTe.

Specimens (12 mm × 4 mm × 2 mm) were removed from the zone-melted ingot and annealed at 630°C under various pressures of mercury for 10 days. Two furnaces were used, one of which controlled the mercury pressure and the other of which provided the annealing temperature of the sample. Initially, specimens were quenched in water from the annealing temperature. However, it was observed that blisters appeared on the surface and small holes extended throughout the bulk of quenched specimens. One possible explanation of these observations is that weakly bonded mercury in the specimen explodes out of the specimen as a result of the severe pressure change occurring at the specimen surface upon quenching. This hypothesis was shown to be correct by subsequent experiments. The specimens of HgTe were cooled slowly from temperature under the condition that the vapor pressure of mercury over the specimen be equal to half the vapor pressure of mercury at the specimen temperature. With these cooling conditions, annealed specimens do not possess surface blisters or small pores.

As shown in the next section, the samples annealed under a pressure of 10 atmospheres of mercury were *p*-type. As the mercury pressure was increased to 15·5 atm, extrinsic hole density decreased. The results show quite conclusively that the composition near stoichiometry of HgTe can be controlled by annealing in mercury vapor.

ELECTRICAL PROPERTIES OF MERCURY TELLURIDE

The Hall coefficient as a function of temperature of an unannealed, zone-melted specimen and three annealed specimens is shown in Fig. 3. From the measured Hall coefficient in the extrinsic region, R_{ext}, and the Hall maximum, R_{max}, on Specimen 5F, the average actual hole to electron mobility ratio, b, was determined to be 0·01 using the equation, $R_{\text{max}}/R_{\text{ext}} = (1-b)^2/4b$. Using this mobility ratio and the conditions that $n_e = n_h b$ at the Hall maximum and $n_e = n_h b^2$ at the Hall null, where n_e and n_h are the electron and hole concentrations, respectively, an energy gap of approximately 0·01 eV is calculated. However, the assumption that the actual electron mobility is always one hundred times greater than the actual hole mobility between the temperature of the Hall crossover, 75°K, and the temperature of the Hall maximum, 250°K, could be in considerable error. Hence, the validity of this method for determining the energy gap of HgTe is uncertain.

In Fig. 4, the resistivity as a function of temperature is given for several specimens of HgTe. Specimens 3A and 5C, which were *n*-type over the measured temperature range, have considerably lower resistivities than the *p*-type Specimens 5E and 5F. The behavior is consistent with the low value of the hole-to-electron mobility ratio. From the data on resistivity as a function of temperature for *p*-type Specimen 5F, a value for the energy gap, ΔE, of 0·08 eV was obtained by use of the equation $1/\rho = Ae^{-\Delta E/2kT}$. This value is identical to that given in early Russian literature.(2) However, since the electron mobility does

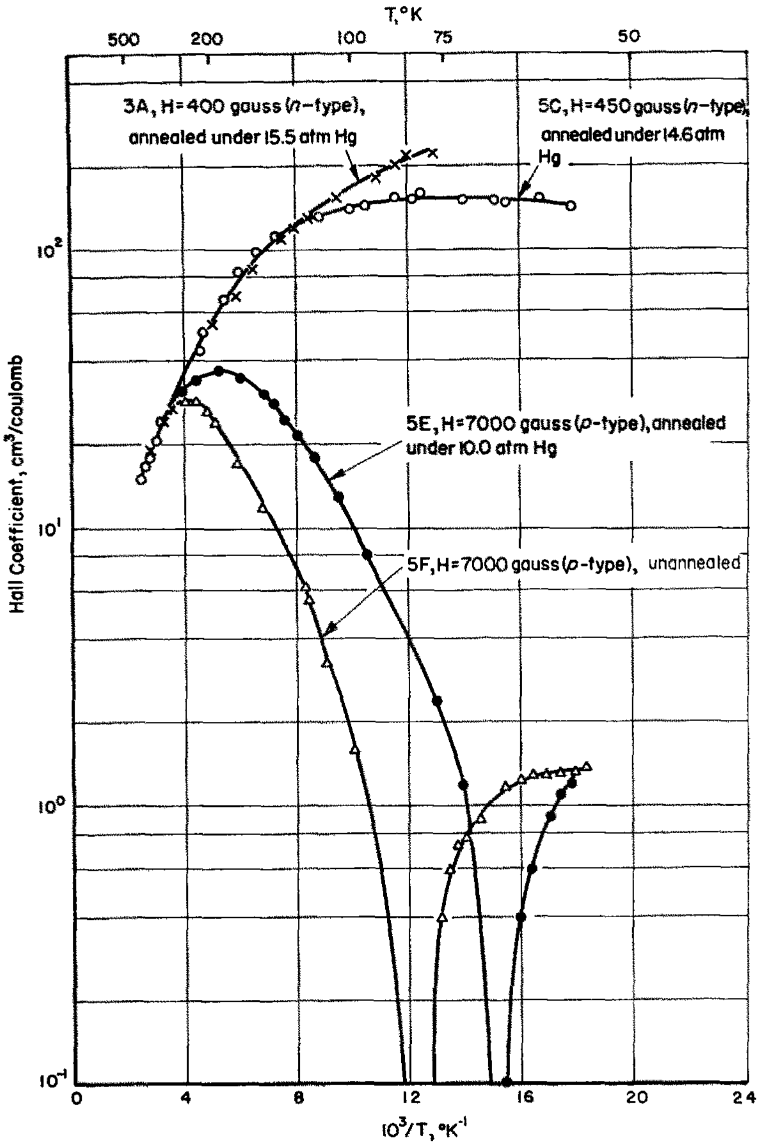

FIG. 3. Hall coefficient as a function of reciprocal temperature for two n-type and two p-type specimens of HgTe.

not vary as $T^{-3/2}$ in the measured temperature interval, the above equation leads to an erroneous energy gap value.

In Fig. 5, the Hall mobility as a function of temperature is shown for the four specimens of HgTe. It is seen that the mobility varies as $T^{-\alpha}$ from 350°K to 55°K where $\alpha \leqslant 1$. Also, the electron mobility is quite high. A value of 17,000 cm^2/Vsec at room temperature and a value of 25,000 cm^2/Vsec at 143°K were obtained for the n-type specimens. The ratio of R/ρ for the p-type specimen, 5F, decreases as the temperature decreases due to hole as well as electron conduction playing a role. For the n-type specimens above

200°K, the ratio of R/ρ represents the electron mobility because, although the number of holes and electrons are equal, the hole conductivity is negligible compared to the electron conductivity due to the small value of b. It also follows that since b is small, the density of intrinsic carriers, n_i, is given by $n_i = 1/R_i e$ and since $n_i/T^{3/2} = Be^{-\Delta E/2kT}$, a plot of $\ln 1/R_i T^{3/2}$ vs. $1/T$ should be linear and yield an accurate value of the energy gap.

Fig. 6 shows $1/R_i T^{3/2}$ vs. $10^3/T$°K for the specimens 3A and 5C. From the straight line portion of the curve, an energy gap of 0·02 eV was calculated. This value is in good agreement with the value of 0·025 eV given by TSIDILKOVSKII.(5) The work of CARLSON(6) and BLACK *et al.*(3) also yields an energy gap of 0·025 eV. The deviation from the straight line below 200°K is believed to be due to the onset of extrinsic conduction while the deviation above room temperature is indicative of degeneracy.

Fig. 7 shows the Hall coefficient as a function of temperature for specimens 3A and 5C measured at magnetic fields of approximately 400 gauss and 7000 gauss. The two-band model of an intrinsic semiconductor appears to explain qualitatively the dependence of Hall coefficient on magnetic field from the highest temperature at which measurements were carried out to a temperature of about 140°K. The variation of Hall coefficient with magnetic field at lower temperatures is not understood.

Fig. 8 shows the Hall coefficient as a function of temperature for two p-type specimens of HgTe. At the Hall maximum for specimen 5F, it is seen that the Hall coefficient increases from 28 cm^3/coulomb at 7000 gauss to 32 cm^3/coulomb as the magnetic field is decreased to 400 gauss. Also, from the figure it is seen that the temperature of the Hall crossover increases as the magnetic field is increased. This behavior is analogous to that found in p-type InSb(7) but opposite to that observed in p-type germanium.(8) The InSb data is consistent with results due to contributions from one high-mobility electron and one or more holes of lower mobility, while the explanation of the germanium behavior(8) requires a high-mobility hole, an intermediate-mobility electron and a low-mobility hole.

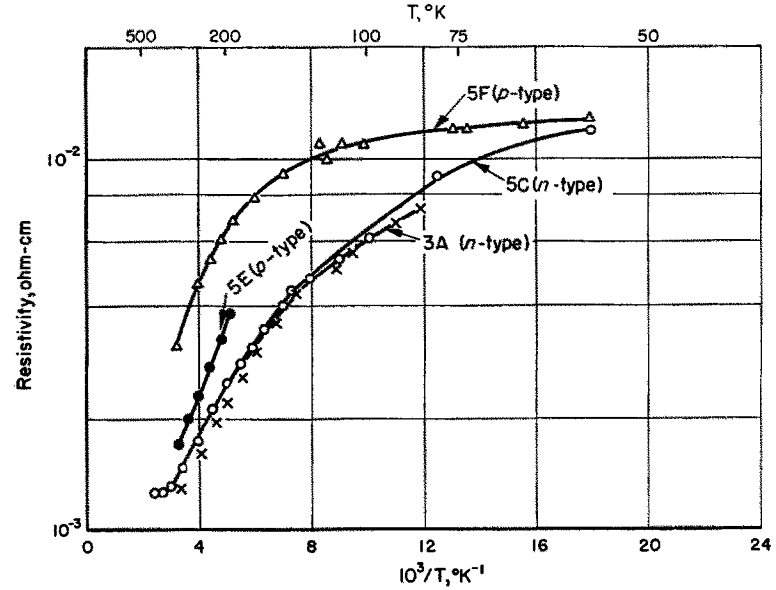

FIG. 4. Resistivity as a function of reciprocal temperature for two n-type and two p-type specimens of HgTe.

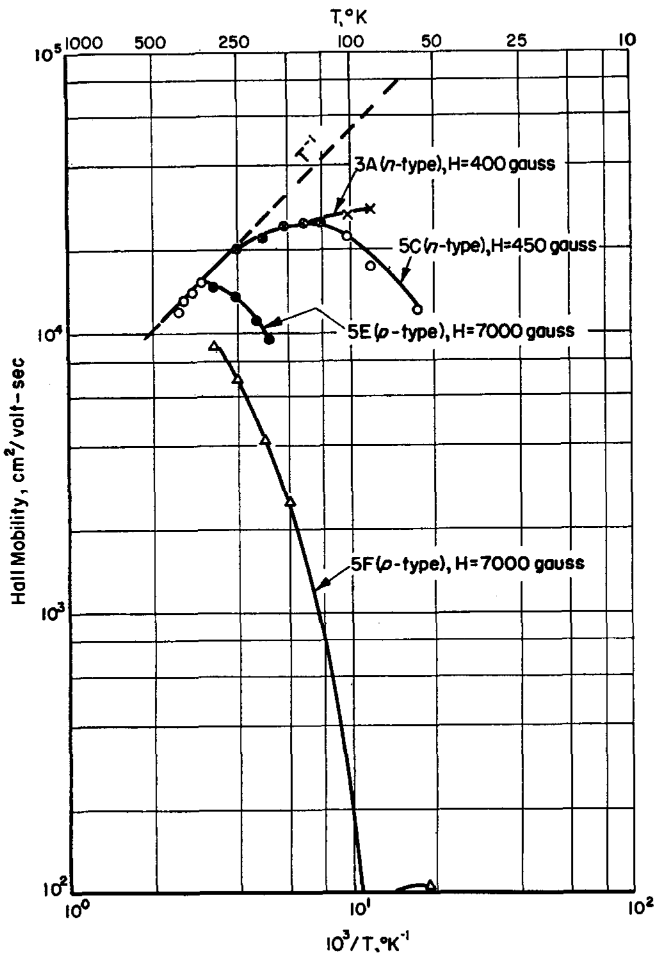

FIG. 5. Hall mobility as a function of reciprocal temperature for two *n*-type and two *p*-type specimens of HgTe.

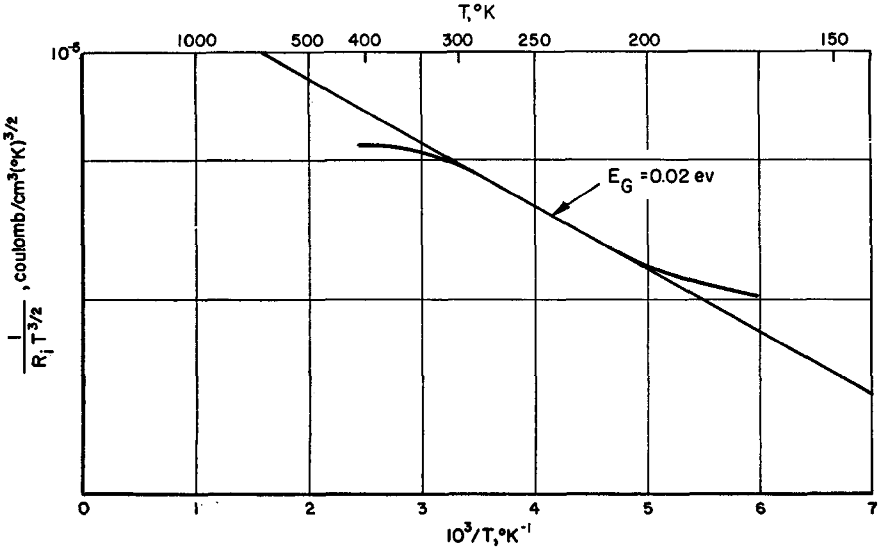

FIG. 6. Reciprocal of the product of temperature to the three-halves power and Hall coefficient as a function of reciprocal temperature for the *n*-type specimens of HgTe.

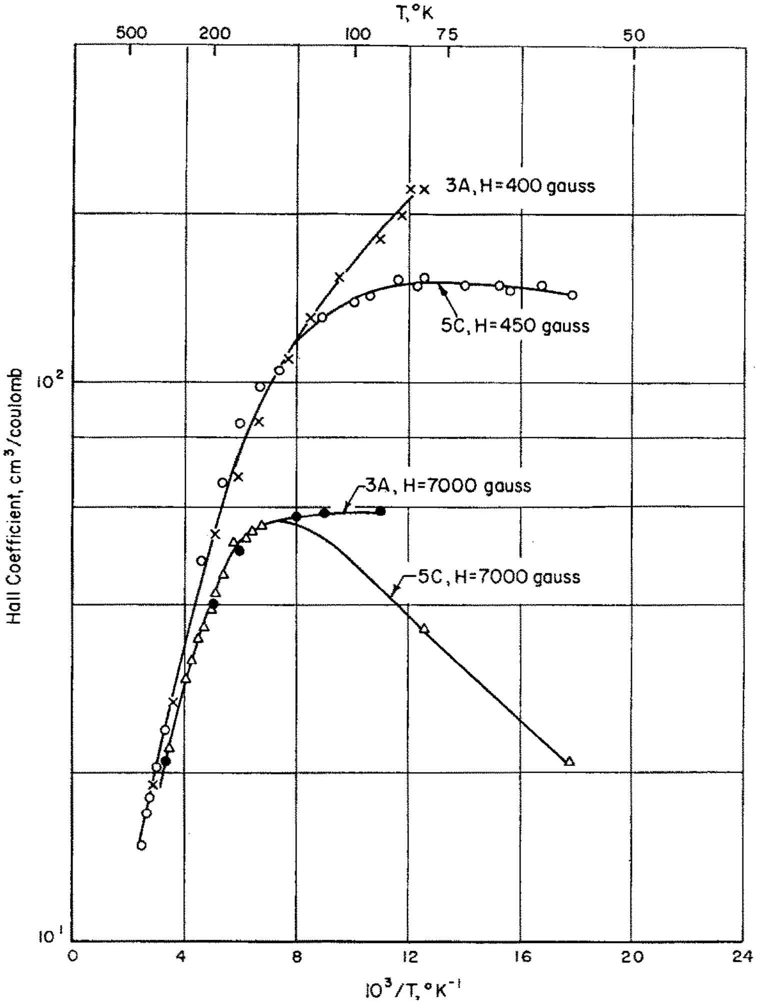

FIG. 7. Hall coefficient as a function of reciprocal temperature for two n-type specimens of HgTe at magnetic fields of approximately 400 gauss and 7000 gauss.

CONCLUSIONS

The compound HgTe can be prepared by direct reaction of liquid tellurium with mercury vapor. By means of a three-temperature-zone apparatus the compound was zone melted. By annealing in mercury vapor the composition of the specimen near stoichiometry can be altered.

It is concluded that the actual hole to electron mobility ratio in HgTe is very small, perhaps the order of 0·01. The energy gap at 0°K is also very small, approximately 0·02 eV. Electron mobilities of 17,000 cm^2/Vsec at room temperature and 25,000 cm^2/Vsec at 143°K have been achieved.

Acknowledgements—The authors gratefully acknowledge helpful discussions with Dr. A. C. BEER. The assistance of Mr. J. I. GENCO in preparing samples is greatly appreciated.

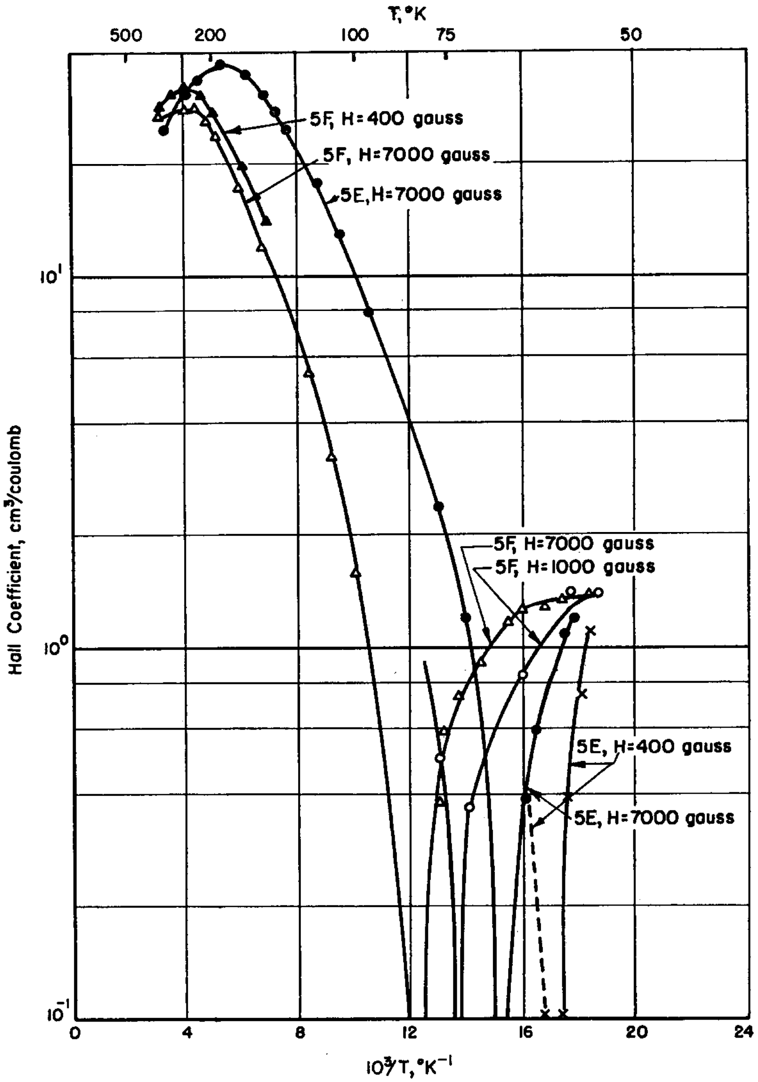

FIG. 8. Hall coefficient as a function of reciprocal temperature for two *p*-type specimens of HgTe for weak magnetic fields and for 7000 gauss.

REFERENCES

1. HARMAN T. C., PARIS B., MILLER S. E. and GOERING H. L. *J. Phys. Chem. Solids* **2,** 181 (1957).
2. MOKROVSKII N. P. and REGEL A. R. *Zh. tech. fiz. USSR* 22, 8, 1281 (1952).
3. BLACK J., KU S. and MINDEN H. *J. Electrochem. Soc.* To be published.
4. KROGER F. A. and DENOBEL D. *J. Electronics* **1,** 190 (1955).
5. TSIDILKOVSKII I. M. *Zh. tech. fiz. USSR* **27,** 1744 (1957).
6. CARLSON R. O. To be published.
7. HARMAN T. C., WILLARDSON R. K. and BEER A. C. *Phys. Rev.* **95,** 699 (1954).
8. WILLARDSON R. K., HARMAN T. C. and BEER A. C. *Phys. Rev.* **96,** 1512 (1954).