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Anomalous Thermoelectric Power as Evidence for Two-Valence Bands in SnTe

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The thermoelectric power (α) of p-type SnTe has been measured between room temperature and 450°C for apparent hole concentrations ($p^*=1/eR_{300}$) between 1×10^{20} and 1.8×10^{21} cm^{-3}. At room temperature, α does not decrease monotonically with increasing p^* in the usual manner for a p-type semiconductor. Instead, it increases from 5–8 μV/deg at $p^*=1$–2×10^{20} cm^{-3} to a maximum of 34μV/deg at $p^*=8\times10^{20}$ cm^{-3}, after which it decreases to 20.5 μV/deg at $p^*=1.8\times10^{21}$ cm^{-3}. The maximum gradually disappears with increasing temperature. At 400 and 450°C, α decreases monotonically with increasing p^*. By means of numerical calculations for a particular set of band parameters, it is shown that this type of anomalous variation in α can be exhibited by a p-type semiconductor with two nondegenerate valence bands. It is found that the observed properties of SnTe, including the variation of Hall coefficient with temperature and carrier concentration, are qualitatively consistent with a two-valence-band model, but are difficult to explain on the assumption that SnTe is a semimetal. However, it has not been possible to obtain a quantitative fit to the data with a two-band model in which both bands are of simple parabolic form.

INTRODUCTION

ALL reported samples of SnTe are strongly p type, with apparent carrier concentrations ($p^*=1/eR_H$) at 300°K varying from 10^{20} to 2×10^{21} cm^{-3}.[1–8] Several investigations of the composition stability limits of SnTe have shown that for undoped samples the observed differences in p^* result from differences in stoichiometry. For single crystals saturated at 600°C with Sn or Te, Houston, Bis, and Gubner[2] obtained p_{300}^* values of 2×10^{20} and 2×10^{21} cm^{-3}, respectively. Our experiments[3] show that the composition of single crystals annealed at 750°C varies from 50.1 at.% Te for Sn-saturated samples to 50.8 at.% Te for Te-saturated samples. The corresponding values of p_{300}^* are 2.5×10^{20} and 1.3×10^{21} cm^{-3}, respectively. Similar results have been obtained by Mazelsky and Lubell[4] for pressed powders annealed at 500°C. These results indicate that even the lowest carrier concentrations observed in undoped SnTe probably result from the presence of lattice defects (specifically, Sn vacancies[3]) associated with deviations from stoichiometry.

In investigating the stoichiometry of SnTe, we have found[5] that the thermoelectric power at room temperature passes through a maximum with increasing p^*, rather than decreasing monotonically in the usual manner for a p-type semiconductor. This anomalous variation in thermoelectric power was observed independently by Sagar and Miller,[6] who suggested an explanation in terms of a semimetal model for SnTe. In this paper, we demonstrate that this type of behavior can also be exhibited by a p-type semiconductor with two-valence bands. Such a band model was proposed for SnTe by Allgaier and Scheie[7] to account for the dependence of Hall coefficient on temperature. We present data for the thermoelectric power of SnTe between room temperature and 450°C, and show that these data are qualitatively consistent with a two-band model but are difficult to explain on the assumption that SnTe is a semimetal.

EXPERIMENTAL

Samples 5–10 mm long, 5 mm wide, and 1.5–2 mm thick were cut from undoped or Bi-doped ingots of SnTe. The ingots were grown in quartz boats by a horizontal Bridgman technique from melts made by fusing Sn and Te of 99.999% purity in stoichiometric proportions. The Bi-doped melts contained, in addition, 1.5 or 3 at.% Bi. Undoped samples were single or occasionally bicrystals, as determined by etching, while Bi-doped samples contained 5 to 15 grains. Measurements were made on (a) as-grown samples, (b) samples annealed between 550 and 790°C in the presence of Sn-Te ingots of various compositions, in order to vary their stoichiometry, and (c) Cu-doped samples prepared from as-grown or annealed samples by Cu-plating and annealing at 500°C under hydrogen for 20–40 h. Details of ingot preparation and sample treatment are described elsewhere in a paper on the stoichiometry of SnTe.[3]

Measurements of the Hall coefficient at 6 kG and electrical resistivity were made on all samples at 300 and 77°K by conventional dc methods. The Hall voltages, which were of the order of 1 μV, were measured with a Leeds and Northrup dc amplifier whose output was read with a Sargent recording potentiometer. A maximum sensitivity of 0.025 μV/mm on the recorder chart can be attained in this manner.

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* Operated with support from the U. S. Army, Navy, and Air Force.

[1] K. Hashimoto and K. Hirakawa, J. Phys. Soc. Japan **11**, 716 (1956).

[2] B. B. Houston, R. F. Bis, and E. Gubner, Bull. Am. Phys. Soc. **6**, 436 (1961).

[3] R. F. Brebrick, J. Phys. Chem. Solids **24**, 27 (1963).

[4] R. Mazelsky and M. S. Lubell (to be published).

[5] R. F. Brebrick and A. J. Strauss, Bull. Am. Phys. Soc. **7**, 203 (1962).

[6] A. Sagar and R. C. Miller, Bull. Am. Phys. Soc. **7**, 203 (1962).

[7] R. S. Allgaier and P. O. Scheie, Bull. Am. Phys. Soc. **6**, 436 (1961).

[8] R. S. Allgaier and B. B. Houston, in *Proceedings of the 1962 International Conference on Physics of Semiconductors, Exeter*, edited by A. C. Stickland (The Institute of Physics and The Physical Society, London, 1962).

The thermoelectric power (α) at 300°K was also measured for all samples. The measurements were made with a small vise-like apparatus consisting of two iron jaws with an iron-constantan thermocouple junction soldered to the face of each jaw. The thermocouple lead wires were passed through holes drilled in the jaws. Clamping a sample in the vise produced good thermal and electrical contact between the thermocouples and the ends of the sample. One jaw was heated to maintain a temperature difference of 3–6°C across the sample. Voltages were measured to $\pm 0.25\ \mu$V with a Leeds and Northrup K-3 potentiometer. The measurements gave α for SnTe with respect to iron. Absolute values of α for SnTe were obtained by subtracting the absolute thermoelectric power of iron at 300°K, 11 μV/deg.

The thermoelectric power of selected samples was measured between room temperature and 450°C by means of a second apparatus. The sample was clamped vertically between two platinum disks 0.025 in. thick and $\frac{7}{8}$ in. in diameter which were supported by silver blocks $\frac{1}{2}$ in. thick and $\frac{7}{8}$ in. in diameter. Quartz wool was packed around the sample in order to reduce convection currents. A Pt, Pt-13% Rh thermocouple junction was spot-welded to each platinum disk, and the thermocouple lead wires were passed through holes in the silver blocks. Each silver block was mounted on a $\frac{1}{2}$-in.-diam Steatite rod which was fastened in turn to a steel disk $2\frac{1}{2}$ in. in diameter. A resistance heater wound on the upper Steatite rod just above the silver block was used to maintain a temperature difference of about 5–10°C across the sample during the measurements. The apparatus was clamped together by tightening wing nuts on two threaded stainless steel rods 16 in. long which passed through holes in the steel disks. Spring loading was used in order to maintain suitable pressure on the sample at all temperatures. After the apparatus had been assembled, it was lowered into a Pyrex tube inside a 3-in.-i.d. resistance furnace 11 in. long. Nitrogen was slowly passed up through the Pyrex tube throughout each run in order to minimize oxidation of the sample at elevated temperatures.

Power to the resistance furnace was supplied by a Variac, the input to which was stabilized by a Sola constant-voltage transformer. Essentially constant temperatures could be obtained by fixing the Variac output voltage and allowing the system to equilibrate. Measurements under steady-state conditions were made manually, using a K-3 potentiometer as in the room-temperature experiments. Measurements were also made while the temperature was being increased at about 0.5°C/min by slowly increasing the Variac output voltage, using a small dc motor operating through a gear reductor to turn the Variac shaft. For these measurements, a Sargent recording potentiometer was used to determine the four voltages from which the thermoelectric power was calculated: two thermocouple voltages and two voltages across the sample (Pt-sample-Pt and Pt, 13% Rh-sample-Pt, 13% Rh). The difference between each of these voltages and a suitable bucking voltage was measured successively with a Leeds and Northrup dc amplifier whose output was recorded by the Sargent potentiometer. The sensitivity generally used was 0.5 μV/mm on the recorder chart. The bucking voltage for the two thermocouple signals was supplied by a K-3 potentiometer, and the bucking voltage for the two signals across the sample was supplied by a Rubicon type B potentiometer. A Sensitive Research low-thermal emf chopper[9] was used for switching. This chopper, which consists of four double pole double throw switches actuated by the same cam shaft, was driven by a 1 rpm motor. A complete cycle of four voltage measurements, each lasting 15 sec, was completed every minute. It was found that each of the four voltages varied linearly with time over a period of several minutes. Therefore, three successive traces for each voltage were connected by a straight line, and simultaneous values of all four voltages were obtained by interpolation. These values were then used to calculate the thermoelectric power. In order to determine the accuracy of this method, it was used on a number of occasions to measure thermoelectric power under steady-state conditions. The measured voltages agreed to better than 1 μV with those obtained manually using the K-3 potentiometer, and the values of α agreed to within 0.1 μV/°C with the manual values. The measurements gave α for SnTe with respect to platinum. Absolute values of α were obtained by subtracting the absolute thermoelectric power of platinum at the appropriate temperature, as given by Nyström.[10]

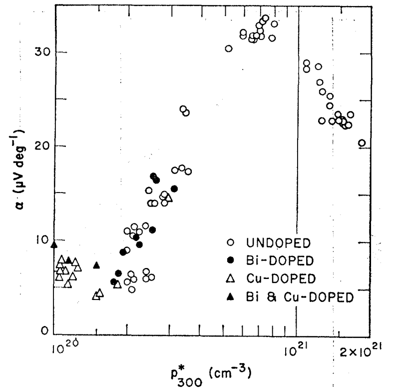

FIG. 1. Variation of thermoelectric power (α) of SnTe at 300°K with apparent carrier concentration ($p_{300}{}^*$).

RESULTS

The absolute thermoelectric power (α) of SnTe at room temperature is shown in Fig. 1 as a function of the apparent carrier concentration at room temperature ($p^* = 1/eR_{300}$). The results are in good agreement with those reported by Sagar and Miller[6] in the concentration range above 2×10^{20} cm^{-3} where the data overlap. The earlier data of Hashimoto and Hirakawa[1] for 3 samples

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[9] T. M. Dauphinee and S. B. Woods, Rev. Sci. Instr. 26, 693 (1955).

[10] J. Nyström, Arkiv. Mat. Astron. Fysik 34A, 1 (1957).

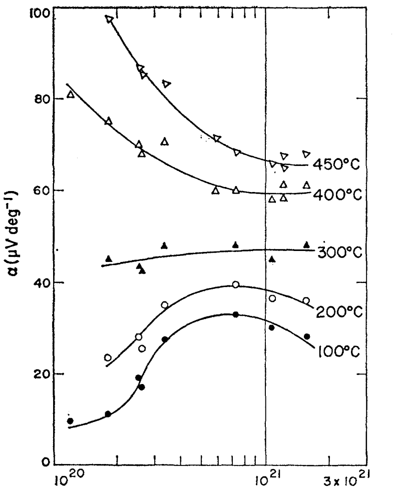

FIG. 2. Variation of thermoelectric power of SnTe with apparent carrier concentration for temperatures between 100 and 450°C.

with p_{300}^* between 5 and 8×10^{20} cm^{-3} also agree with the present results. All values of α are positive, but they do not decrease monotonically with increasing p^* in the usual manner for a p-type semiconductor. For p^* between 1 and 2×10^{20} cm^{-3}, the lowest concentrations obtained, α is independent of p^* within the sample-to-sample scatter. Over this concentration range, almost all the observed values of α are between 5 and 8 μV/deg. As p^* increases above 2×10^{20} cm^{-3}, α increases to a maximum of 34 μV/deg at $p^*=8\times10^{20}$ cm^{-3}, after which it decreases to 20.5 μV/deg at $p^*=1.8\times10^{21}$ cm^{-3}, the highest concentration obtained. For as-grown samples crystallized from stoichiometric melts, α is generally between 31 and 34 μV/deg and p^* between 6 and 8×10^{20} cm^{-3}.

Isotherms of α vs p_{300}^* are given in Fig. 2 for 5 temperatures between 100 and 450°C. For the 3 samples with $p_{300}^*=1.2$, 5.89, and 12.4×10^{20} cm^{-3}, α was measured under steady-state conditions. For the remaining 7 samples, the values of α were obtained by interpolation from smoothed curves of α vs temperature based primarily on drift measurements made in the manner described previously. Smoothed curves for two representative samples, together with the experimental data, are shown in Fig. 3. For all samples, the drift measurements were checked against steady-state measurements at room temperature, at about 220°C, and at about 450°C. In each case, the two values of α agreed to within 1 μV/deg.

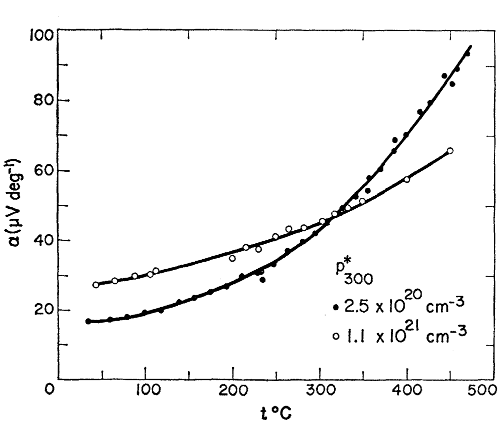

FIG. 3. Variation of thermoelectric power with temperature for two samples of SnTe.

The accuracy of the data for each sample (including those studied only under steady-state conditions) was checked by remeasuring α at room temperature after the measurements at elevated temperatures had been completed. The initial and final values of α agreed to within 1 μV/deg, even for samples held at temperatures between 200 and 300°C for as long as 16 h. Therefore, no significant errors due to oxide formation at the sample-platinum contacts or to irreversible changes in sample composition could have occurred.

As seen in Fig. 2, the anomalous maximum in α observed at room temperature gradually disappears with increasing temperature. At 300°C, α is independent of p_{300}^* to within ±2.5 μV/deg, and at 400 and 450°C, α decreases monotonically with increasing p_{300}^* in the usual manner. In contrast with the present data, Hashimoto and Hirakawa[1] reported that α became negative at about 250°C for a sample with $p_{300}^*=5.2\times10^{20}$ cm^{-3}. We believe that this result was erroneous.

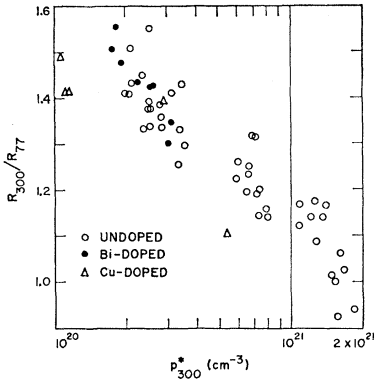

FIG. 4. Variation of Hall coefficient ratio (R_{300}/R_{77}) of SnTe with apparent carrier concentration.

The results of Hall measurements on the SnTe samples are shown in Fig. 4, where R_{300}/R_{77} is plotted against p_{300}^*. For the lowest values of p_{300}^*, R_{300} is significantly greater than R_{77}, as reported by Allgaier and Scheie[7] and by Sagar and Miller.[6] The ratio R_{300}/R_{77} decreases monotonically with increasing p_{300}^*. At the highest concentrations, $R_{77}\simeq R_{300}$.

The Hall mobilities for the SnTe samples are shown in Fig. 5, where $(R\sigma)_{300}$ and $(R\sigma)_{77}$ are plotted against p_{300}^* and p_{77}^*, respectively. The values agree with those reported[7,8] for single-crystal samples. At both temperatures, the mobility decreases monotonically with increasing p^*. The data, including those for Cu-doped samples with the lowest p^* values, are seen to be well represented by straight lines on a log-log plot.

Copper acts as a donor in SnTe. In order to obtain SnTe samples with low-carrier concentrations, Sn-saturated crystals with p_{300}^* between 2.0 and 2.5×10^{20} cm^{-3} were doped with Cu by diffusion at 500°C from a layer of Cu electroplated on the sample surface. The number of Cu atoms deposited was calculated from the total charge passed during electroplating. This number was divided by the sample volume to obtain an average Cu concentration ($\bar{C}$). The reduction in carrier concentration produced by Cu doping is shown in Fig. 6, where the differences between the initial and final values of p_{300}^* and p_{77}^* are plotted against $\bar{C}$. Although there is considerable scatter in the data, the results are represented fairly well by the expressions $\Delta p_{77}^* = 1.1\bar{C}$ and $\Delta p_{300}^* = 0.7\bar{C}$ for values of $\bar{C}$ up to 1.5×10^{20} cm^{-3}. For higher values of $\bar{C}$, Δp_{77}^* and Δp_{300}^* appear to be constant within the accuracy of the data. This result indicates that the solubility of Cu in Sn-saturated SnTe at 500°C is about 1.5×10^{20} cm^{-3}.

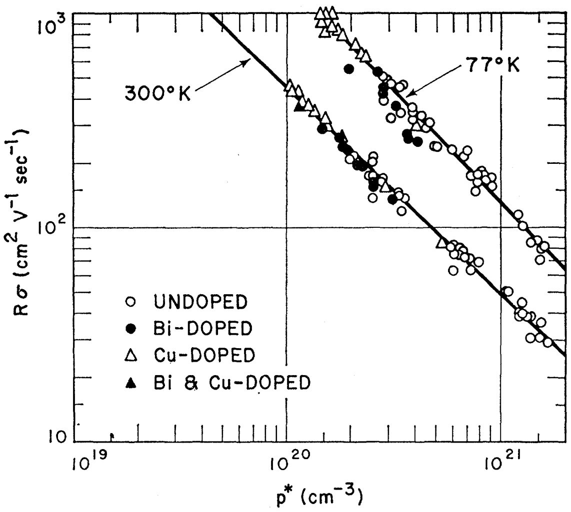

FIG. 5. Variation of Hall mobility ($R\sigma$) of SnTe with apparent carrier concentration at 300 and 77°K.

DISCUSSION

A. Two-Valence-Band Model

In this section we consider the thermoelectric power of a semiconductor whose electrical conductivity is due entirely to holes which are distributed between two nondegenerate valence bands. It is shown that the thermoelectric power can increase to a maximum with increasing apparent carrier concentration (p^*), although the thermoelectric power associated with each band decreases in the usual manner with increasing concentration. This is accomplished by showing that such a maximum is obtained when the thermoelectric power is calculated numerically for a particular set of band parameters. No attempt is made to establish the general relationships between band parameters which are required for obtaining a maximum. Applicability of the two-band model to SnTe is discussed in the following section.

The thermoelectric power α of a two-band semiconductor is given by

$$\alpha = (\alpha_L\sigma_L + \alpha_U\sigma_U)/(\sigma_L + \sigma_U),$$

where σ is the electrical conductivity, and the subscripts L and U refer to the bands of lower and higher energy, respectively. This expression may be rewritten as follows in terms of the conductivity ratio $y = \sigma_L/\sigma_U$

$$\alpha = (\alpha_L y + \alpha_U)/(1+y). \tag{1}$$

In order to find the dependence of α on carrier concentration, α was first calculated according to Eq. (1) as a function of the reduced Fermi level, $\eta = (\mathcal{E}_F - \mathcal{E}_L)/kT$, where $\mathcal{E}_F$ is the Fermi energy and $\mathcal{E}_L$ is the bottom of the lower valence band. It was assumed that both bands are spherical and parabolic, and that the relaxation time for each band is given by $\tau = \tau_0\mathcal{E}^r$, where $\mathcal{E}$ is the energy of the carriers relative to the bottom of the band in question. The scattering parameter r was taken to be $-\frac{1}{2}$ for both bands. Under these conditions

$$\alpha_L = \frac{k}{e}\left\{2\frac{F_1(\eta)}{F_0(\eta)} - \eta\right\}, \tag{2}$$

$$\alpha_U = \frac{k}{e}\left\{2\frac{F_1(\eta-\Delta)}{F_0(\eta-\Delta)} - (\eta-\Delta)\right\}, \tag{3}$$

where F_0 and F_1 are Fermi integrals[11] and Δ is the reduced-energy difference between the bottoms of the two bands,

$$\Delta = (\mathcal{E}_U - \mathcal{E}_L)/kT.$$

The conductivity ratio y is equal to $p_L\mu_L/p_U\mu_U$, where p is the number of holes and μ is the drift mobility.

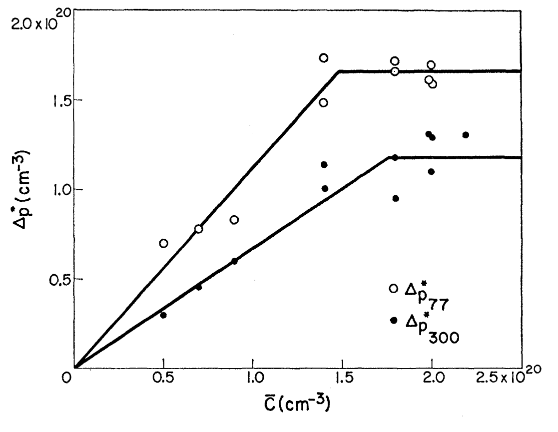

FIG. 6. Change in apparent carrier concentration at 300 and 77°K (Δp^*) as a function of average copper concentration ($\bar{C}$).

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[11] J. Tauc, *Photo and Thermoelectric Effects in Semiconductors* (Pergamon Press, Inc., New York, 1962), Chap. 1.

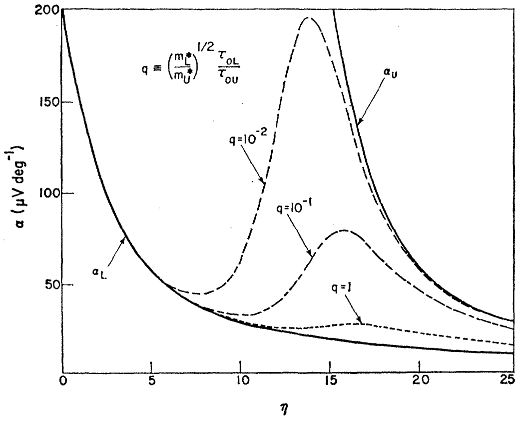

FIG. 7. Variation of thermoelectric power with Fermi level (η) calculated according to the two-valence-band model, assuming spherical parabolic bands, scattering parameter $r=-\frac{1}{2}$, and energy separation of 15 kT between the bands. The solid lines give the thermoelectric power for the lower and upper bands (α_L and α_U, respectively). The dashed lines give the total thermoelectric power.

According to the present model, y is given by

$$y=\frac{F_{1/2}(\eta)}{F_{1/2}(\eta-\Delta)}\left(\frac{m_L^*}{m_U^*}\right)^{3/2}\frac{\mu_L}{\mu_U}=\frac{F_0(\eta)}{F_0(\eta-\Delta)}\left(\frac{m_L^*}{m_U^*}\right)^{1/2}\frac{\tau_{0L}}{\tau_{0U}},$$

where $F_{1/2}$ is a Fermi integral and m^* is the effective mass of holes. Substituting the parameter $q=(m_L^*/m_U^*)^{1/2}(\tau_{0L}/\tau_{0U})$ gives

$$y=qF_0(\eta)/F_0(\eta-\Delta). \tag{4}$$

Values of α for η between 0 and 25 have been calculated according to Eqs. (1)–(4) by assuming that $\Delta=15$. Alternate calculations were made for $q=10^{-2}$, 10^{-1}, and 1. The results are shown in Fig. 7, which also includes the calculated values of α_L and α_U. Although both α_L and α_U decrease monotonically with increasing η, α exhibits a pronounced maximum for both $q=10^{-2}$ and $q=10^{-1}$.

The behavior of α can be explained qualitatively in terms of the dependence of $Q=F_0(\eta)/F_0(\eta-\Delta)$ and $y=qQ$ on η. For sufficiently low values of η, when the Fermi level lies far below the bottom of the upper valence band, the value of Q is so great that $y\gg1$, even for small values of q. In this region, p_L is so large compared to p_U that the upper band makes no appreciable contribution to the conductivity. Consequently, $\alpha_L y\gg\alpha_U$, even though α_U is much greater than α_L. It follows from Eq. (1) that in this region $\alpha=\alpha_L$, and α, therefore, decreases with increasing η.

As η increases, however, Q decreases and p_L/p_U and y decrease. When the Fermi level rises far enough, the proportion of carriers in the upper band becomes sufficient for the upper band to begin to contribute to α, since α_U is no longer negligible compared to $\alpha_L y$. For small values of q, this occurs for values of η at which α_U is still much greater than α_L. In this case, the relative contribution of the upper band can increase rapidly enough with η to cause an increase in α, in spite of the decrease in both α_L and α_U. Eventually, however, the rate of increase in the relative contribution of the upper band must decrease. Then α passes through a maximum and once more decreases like α_L and α_U. In the extreme case, when q is sufficiently small, y becomes so small compared to 1 that $\alpha\approx\alpha_U$. This may be seen in Fig. 7 for $q=10^{-2}$.

Since both p_L and p_U increase monotonically with increasing η, the total carrier concentration, $p=p_L+p_U$, also increases in this manner. It follows from Fig. 7 that α passes through a maximum with increasing p. For a two-band semiconductor, however, p is not, in general, equal to the apparent carrier concentration ($p^*=1/eR_H$). In order to determine the variation of α with p^* for one particular set of parameters, R_H has been calculated as a function of η for $T=300$°K, $\Delta=15$, $(m_L^*)^{3/2}=0.05$, $(m_U^*)^{3/2}=2.5$, and $\tau_{0L}/\tau_{0U}=0.368$. For this choice of effective masses and (τ_{0L}/τ_{0U}), the parameter $q=10^{-1}$. The value of R_H was calculated from the two-carrier expression

$$R_H=\frac{1}{e}\frac{s_L n_L b^2+s_U n_U}{(n_L b+n_U)^2},$$

where s is the ratio of Hall-to-drift mobility, $b=\mu_L/\mu_U$, and these quantities are functions of η.[11] The carrier concentrations p_L and p_U were evaluated according to the equations

$$p_L=\frac{4\pi(2kT)^{3/2}}{h^3}(m_L^*)^{3/2}F_{1/2}(\eta),$$

$$p_U=\frac{4\pi(2kT)^{3/2}}{h^3}(m_U^*)^{3/2}F_{1/2}(\eta-\Delta).$$

By comparing the values of R_H and α calculated at corresponding values of η, the curve of α vs p^* shown

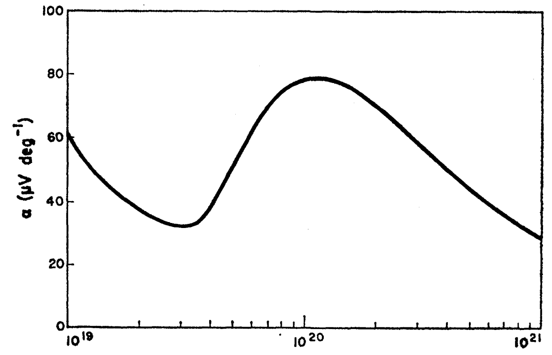

FIG. 8. Variation of thermoelectric power at 300°K with apparent carrier concentration calculated according to the two-valence band model. In addition to making the assumptions listed in the caption for Fig. 7, it was assumed that $(m_L^*)^{3/2}=0.05$, $(m_U^*)^{3/2}=2.5$, and $\tau_{0L}/\tau_{0U}=0.368$.

in Fig. 8 was constructed. It is seen that α passes through a maximum with increasing p^*.

B. Band Structure of SnTe

Two alternative models have been proposed for the band structure of SnTe: the two-valence-band model suggested by Allgaier and Scheie[7] and the semimetal model proposed by Sagar and Miller.[6] In this section we consider how well each of these models accounts for the observed properties of SnTe.

According to the two-valence-band model, as described above, the anomalous variation in α with p^* occurs because for certain values of p^* the two valence bands both make appreciable contributions to α. The semimetal model also explains the variation in α in terms of two bands, in this case the valence and conduction bands. According to this model, the thermoelectric power of SnTe is given by the usual expression $\alpha=(\alpha_p\sigma_p+\alpha_n\sigma_n)/\sigma$, where the subscripts p and n refer to the valence and conduction bands, respectively. For the highest values of p^*, the concentration of electrons in the conduction band is so small that $\sigma_p \gg \sigma_n$ and $\alpha_p\sigma_p \gg \alpha_n\sigma_n$. Consequently, $\alpha=\alpha_p$, and α increases with decreasing p^* in the usual manner for a one-carrier material. As p^* continues to decrease, however, the concentration of intrinsic electrons eventually increases enough for $\alpha_n\sigma_n$ to become appreciable compared to $\alpha_p\sigma_p$. Since α_n is negative, α begins to decrease with decreasing p^*, although α_p continues to increase. This explanation requires SnTe to be a semimetal, since only in a semimetal would the intrinsic carrier concentration be high enough at 300°K for there to be appreciable concentrations of electrons in the presence of hole concentrations exceeding 10^{20} cm^{-3}.

Although the occurrence of a maximum in α with decreasing p^* is consistent with both band models, differences would be expected in the behavior of α as p^* continues to decrease. As illustrated by Fig. 8, the two-valence-band model predicts that α passes through a minimum and then increases in the usual manner for a one-carrier material, since for sufficiently low hole concentrations $\alpha=\alpha_L$. According to the semimetal model, on the other hand, α would probably pass through zero and become negative, since the concentration of intrinsic electrons might be expected to increase sufficiently for $\alpha_n\sigma_n$ to become larger than $\alpha_p\sigma_p$. Observation of negative values for α at carrier concentrations of about 10^{20} cm^{-3} would, therefore, be excellent evidence for the semimetal model. No negative values have been observed, however. Although failure to obtain negative values might be due to the unavailability of SnTe samples with sufficiently low values of p^*, the data of Fig. 1 indicate that α is no longer decreasing at concentrations below about 2×10^{20} cm^{-3}. These data, therefore, favor the two-valence-band model, although they cannot be regarded as conclusive.

The present data on the temperature dependence of α (Fig. 2) also appear to support the two-valence-band model. According to this model, at constant temperature α rises to a maximum in the concentration region where the proportion of holes in the upper valence band becomes sufficient for the upper band to make an appreciable contribution to α. With increasing temperature, the total hole concentration in each sample remains constant, but the proportion of holes in the upper band increases because the reduced energy difference between the bands, $(\mathcal{E}_U-\mathcal{E}_L)/kT$, decreases. Consequently, the maximum in α would be expected to shift to lower total concentrations as the temperature increases. Therefore, it is reasonable to suppose that maxima were not observed at temperatures of 300°C and above because the maxima at these temperatures occur at concentrations below those in the SnTe samples studied. Failure to observe the maxima at elevated temperatures is not so readily explained by the semimetal model, however. In fact, according to this model, there would be a tendency for the maximum to shift to higher acceptor concentrations with increasing temperature. Such a shift would occur if the intrinsic carrier concentration increased sufficiently to cause a significant increase in the proportion of electrons in each sample, since the decrease in α at constant temperature occurs when the proportion of electrons becomes sufficient for the conduction band to contribute to α. Sagar and Miller[6] have reported a slight shift of this type between 77 and 300°K.

Further evidence supporting the two-valence-band model is provided by the data of Fig. 4 on the temperature dependence of the Hall coefficient. Allgaier and Scheie[7] originally proposed this model for SnTe in order to explain their observation that R_H increases between 77 and 300°K. Two-band models have also been proposed for n-type GaSb,[12] n-type GaAs,[13] and p-type PbTe,[14] each of which exhibits an increase in R_H with temperature over a certain range of temperatures and carrier concentrations. Although a detailed treatment of the problem will not be given here, it may be noted that for constant total hole concentration (p), the minimum value of R_H is obtained when the carriers are all in one band. In this case, the apparent carrier concentration, $p^*=1/R_He$, is equal to p. The maximum value of R_H occurs when the partial conductivities of the two bands are equal ($\sigma_L=\sigma_U$). The observed decrease in R_{300}/R_{77} with increasing hole concentration may be understood by considering the two extreme cases. For the samples with lowest concentrations, at 77°K most of the holes are in the lower band, and $\sigma_L>\sigma_U$. With increasing temperature, holes are transferred to the upper band, σ_U increases relative to σ_L, and R_H increases. For samples with the highest hole concentrations, however, even at 77°K so many of the holes are already in the

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[12] A. Sagar, Phys. Rev. **117**, 93 (1960).

[13] L. W. Aukerman and R. K. Willardson, J. Appl. Phys. **31**, 939 (1960).

[14] R. S. Allgaier, Suppl. J. Appl. Phys. **32**, 2185 (1961).

upper band that $\sigma_U \gg \sigma_L$ and $p^* = p$. Therefore, no significant change in R_H or p^* is observed with increasing temperature. This explanation is consistent with the conclusion that the upper band makes the predominant contribution to the thermoelectric power of high concentration samples.

The semimetal model does not appear to offer a satisfactory explanation of the increase in R_H with temperature. For materials in which all the holes are in a single valence band, there seems to be no reported case in which a positive Hall coefficient increases with temperature. If the electron mobility in such materials is greater than the hole mobility, an increase in negative Hall coefficient with temperature is observed in p-type samples (samples containing excess acceptors) in the region between the temperatures of the Hall zero and the negative Hall maximum. The situation in SnTe would be analogous only in the unlikely case that the samples are actually n type (contain excess donors) and that the hole mobility is greater than the electron mobility.

The present data on Hall mobility as a function of p^* (Fig. 5) and on the effect of copper doping (Fig. 6) appear to be consistent with either of the proposed band models for SnTe. Sagar and Miller[6] obtained shallow minima in their curves of conductivity vs p^* for 77 and 4.2°K, as might be expected on the basis of the semimetal model, but according to the present data, σ_{77} varies monotonically with p^* within the limits of experimental error. It seems reasonable to explain the data on copper doping by assuming that each copper atom incorporated into the SnTe lattice acts as a singly ionized donor and that $p_{77}^* = p$ for hole concentrations below 2.5×10^{20} cm^{-3}. According to the two-valence-band model, the latter assumption implies that for this concentration range, so many of the holes are in the lower band at 77°K that $\sigma_L \gg \sigma_U$. According to the semimetal model, it implies that the proportion of electrons in the conduction band is such that σ_p is much larger than σ_n but that $\alpha_n \sigma_n$ is appreciable compared to $\alpha_p \sigma_p$.

On the basis of the preceding discussion, it seems quite probable that SnTe is a semiconductor with two-valence bands rather than a semimetal. However, while the two-valence-band model accounts qualitatively for the observed properties of SnTe, we have not succeeded in using this model to obtain a quantitative fit to the data for the thermoelectric power and Hall coefficient as functions of carrier concentration and temperature. By adopting suitable band parameters, we have been able to obtain a fair fit for the variation of α with p^* at 300°K, but in order to account for both the very low minimum and relatively high maximum values of α, it was necessary to assume extremely large values for the Fermi level ($\sim 50\ kT$ above the bottom of the lower band at $p^* = 10^{20}$ cm^{-3}) and for the energy difference between the bands ($\sim 90\ kT$). According to calculations based on these values, neither α nor R_H should change appreciably with temperature over the range investigated experimentally, in sharp contrast to the experimental results. Therefore, it seems necessary to conclude that even the two-valence-band model is not sufficiently complex to account for the observed properties of SnTe if the two bands are of simple parabolic form.

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Note added in proof. The results obtained by Sagar and Miller[6] in their investigation of SnTe appear in *Proceedings of the 1962 International Conference on Physics of Semiconductors, Exeter*, edited by A. C. Strickland (The Institute of Physics and The Physical Society, London, 1962).