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IX-7. The Fermi Surface of Tin Telluride: Shubnikov-de Haas Effect

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We have measured the angular dependence of the Shubnikov-de Haas oscillations at 4.2 and 1.3°K in the $(\bar{1}10)$ and (001) planes, the weak-field Hall coefficient at 77°K, and the magnetic field dependence of the Hall coefficient at 4.2°K, on two samples of p-type tin telluride. The carrier concentrations (p) of these samples, obtained from the strong-field Hall coefficient $R_\infty = 1/pe$, were 1.00 and $1.03\times10^{20}\,\mathrm{cm}^{-3}$. A complicated pattern of oscillations was observed at all orientations in each plane of rotation. The frequency spectra of these data were obtained by means of a Fourier analysis. These spectra show that there are four extremal cross-sections which minimize when the magnetic field is in a $<111>$ type direction. Consistency with the total carrier concentration suggests that the Fermi surface consists of four $<111>$ prolate surfaces with multiple extrema.

§ 1. Introduction

Tin Telluride (SnTe) is an extrinsic p-type semiconductor[1,2] having the sodium chloride structure. Large deviations from stoichiometry result in high carrier concentrations (p) in the range 10^{19} to $10^{21}\,\mathrm{cm}^{-3}$. The mobility is a strong function of the number of vacancies in the tin sublattice and is unusually high in the presence of so many defects.[3] The results of electrical,[4~7] elastic[8] and optical[9] measurements on SnTe are very unusual and difficult to understand. Each of these measurements points to the existence of a complicated band structure.

Because of a combination of high magnetic fields and high mobilities, we have been able to observe Shubnikov-de Haas oscillations in the magnetoresistance of SnTe. According to the theory[10] of this effect, the frequency (reciprocal of the period) of an oscillation is given by

$$F=(ch/2\pi e)A\ , \qquad (1)$$

where A is the extremal cross-section of the Fermi surface perpendicular to the direction of the magnetic field. The units of F and A are respectively Gauss and cm^{-2}. Thus the shape of the Fermi surface can be directly determined by these measurements.

We have been able to observe these oscillations over a wide range of p, from 5×10^{19} to $5\times10^{20}\,\mathrm{cm}^{-3}$, and we believe that this range can be extended. Thus we are provided with the unique opportunity to investigate changes in the shape of the Fermi surface as the number of carriers is changed over a wide range. In addition, because the lattice constant changes with the number of vacancies in the Sn sublattice, it may be possible to observe and relate changes in band structure produced by changes in lattice constant.

We have previously reported[11] the results of investigations on several samples with $p>1.3\times10^{20}\,\mathrm{cm}^{-3}$. Until now, our analyses have been hindered because of the complicated nature of these results. However, it was possible to show that for p less than about $2\times10^{20}\,\mathrm{cm}^{-3}$, the Fermi surface could be approximated by 4 distorted surfaces located at the L-points of the Brillouin zone. Above this value of p, an additional surface was observed.

§ 2. Present Experiment

In the work to be presented in this paper, we have restricted ourselves to a more detailed investigation of the Fermi surface at one carrier concentration, lower than those previously studied, in order to obtain higher mobilities. In this way, with greater $\omega\tau$'s, we hoped to gain information about the larger cross-sections of the Fermi surface. We measured the angular dependence of the Shubnikov-de Haas oscillations at 4.2°K and 1.3°K by sweeping the magnetic field from 0 to 150 kG at each orientation (the weak-field Hall coefficient at 77°K) and the magnetic field dependence of the Hall coefficient at 4.2°K. The properties of the samples on which these measurements were made are given in Table I.

Table. I. Properties of the p-type SnTe Samples Studied.

Sample No.	Resistivity (ohm·cm) $T=4.2$°K	Hall Mobility ($cm^2/V\cdot sec$) $T=4.2$°K	$1/R_0e$ (cm^{-3}) $T=77$°K	$1/R_\infty e$ (cm^{-3}) $T=4.2$°K
669	0.951×10^{-5}	5,017	1.31×10^{20}	1.00×10^{20}
670	1.002×10^{-5}	4,804	1.30×10^{20}	1.03×10^{20}

R_0 and R_∞ are respectively the weak- and strong-field Hall coefficients. The magnetic field dependence of the Hall voltage for Sample 670, is shown in Fig. 1. The Hall coefficient at a given field is proportional to the slope of the line from the origin to the point on the curve corresponding to that field. We have assumed that the limiting behavior of the Hall coefficient at high fields, R_∞, is given by the slope of the linear portion of the curve. We then used R_∞ to calculate the carrier concentration.

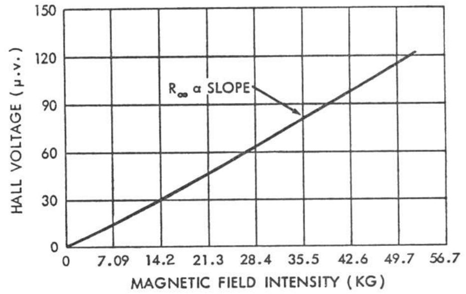

Fig. 1. Magnetic field dependence of the Hall voltage. $T=4.2$°K. The slope of the linear portion of the curve was used to determine $p=1/R_\infty e$.

The angular dependence of the Shubnikov-de Haas oscillations was obtained at 2.5 degree intervals in two planes of rotation. These oscillations began slightly below 30 kG, were observed in all orientations of the magnetic field, and contained more structure than found in samples with higher p. Figure 2 shows the results obtained with the magnetic field in the [111] direction. No obvious simplification of this pattern was observed in any of the high symmetry directions. At 1.3°K a small amount of additional structure is observed and the amplitude of the oscillations at the low field end are slightly enhanced. This small effect of lowering the temperature shows that collision broadening of the Landau levels by the lattice defects is the predominant damping mechanism in SnTe.

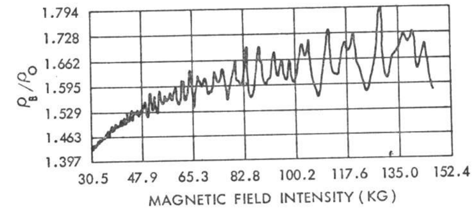

Fig. 2. Resistivity ratio versus magnetic field intensity. Magnetic field direction: [111], $p=1.03\times10^{20}$ cm^{-3}, $T=4.2$°K.

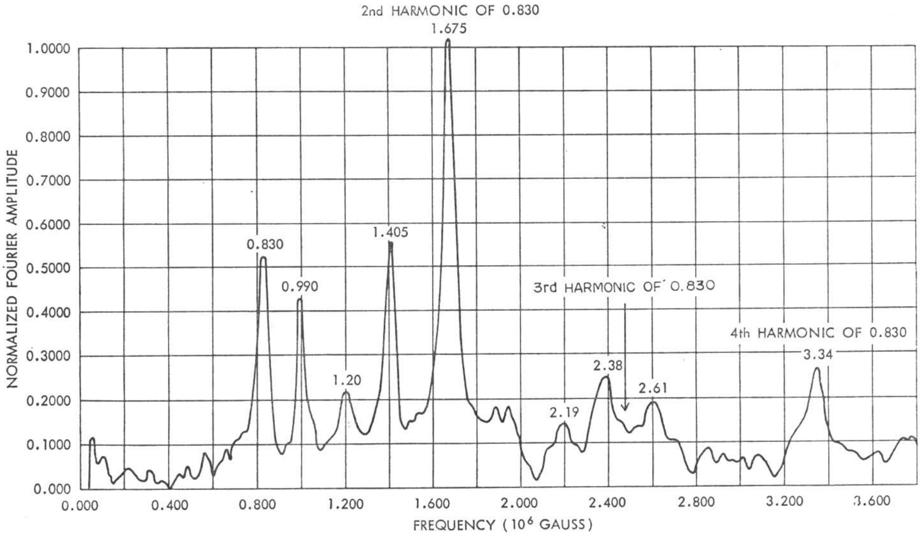

Fig. 3. Fourier analysis of the data shown in Fig. 2.

§ 3. Method of Analysis

Analysis of data obtained prior to the present set of experiments was carried out in the conventional manner of looking for peaks belonging to the same oscillation and counting the number in a given $1/B$ interval. This procedure is difficult and inaccurate in SnTe because of the complicated nature of the data of which Fig. 2 is typical. In addition, because of the large number of frequencies present, it is necessary to obtain data at many orientations in order to follow the angular dependence of each cross-section. This requires that for a rotation over 90 degrees at least 36 traces such as Fig. 2 must be taken. The task of separating out the component frequencies in so many traces with the necessary accuracy is a formidable one. We have recently completed a program for the I. B. M. 7090 computer which enables us to Fourier analyse the oscillatory component of the magnetoresistance. The program first computes a center-line by making a least squares fit of a low order polynomial to the data. This center-line is then subtracted from the data and the remaining oscillatory component is Fourier analysed as a function of $1/B$. The amplitudes are then plotted on a Calcomp plotter. The program has been checked by using it on synthesized data and on raw data which had been analysed by other methods. Figure 3 gives the results of the analysis of the oscillatory component of the data in Fig. 2.

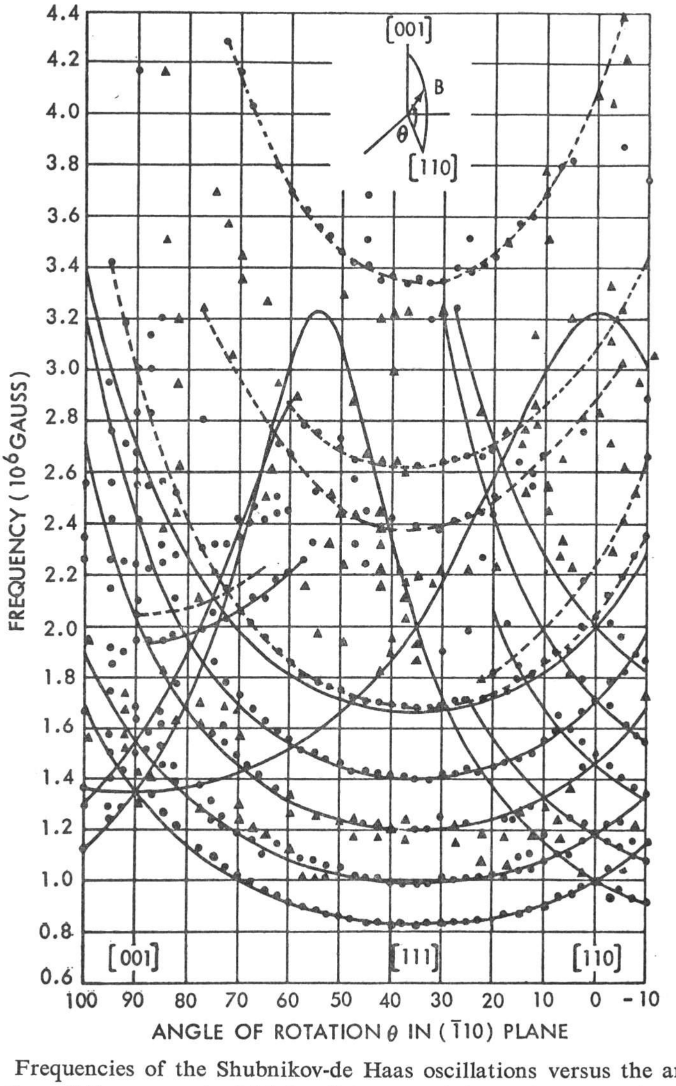

Fig. 4. Frequencies of the Shubnikov-de Haas oscillations versus the angle of rotation of the magnetic field B. B is rotated from [110] to [001].

§ 4. Results

The results obtained by this analysis on Sample 670 for two planes of rotation are given in Figs. 4 and 5. The points plotted correspond to those spectral lines in the Fourier analysis that were sufficiently above the noise level to be reliable. The circles correspond to the strongest lines observed. The most important feature is that the smallest cross-sections occur when the magnetic field is in the [111] direction. This shows that the corresponding surfaces are elongated in that direction. This result was also characteristic of data obtained on samples of higher p. In contrast to these earlier results, Fig. 4 shows that there are four extremal cross-sections which minimize when B is parallel to [111]. Only two were observed previously. This difference is more likely due to the larger $\omega\tau$'s obtainable at this p and to the improvement in the method of analysis, than to the appearance of new cross-sections. The second and fourth harmonics of the lowest curve are very strong. Three other harmonics are also indicated by the dashed curves.

If we assume that the four curves with minima at [111] are each generated by an ellipsoid of revolution,

$$F=1.46\times10^6\ (p_s/10^{19})^{2/3} \times\frac{K^{1/6}}{[1+(K-1)\cos^2\theta]^{1/2}}\ \text{Gauss}, \qquad (2)$$

where F is the frequency, p_s is the number of carriers enclosed by the ellipsoid, K is the square of the major to minor axis ratio, and θ is the

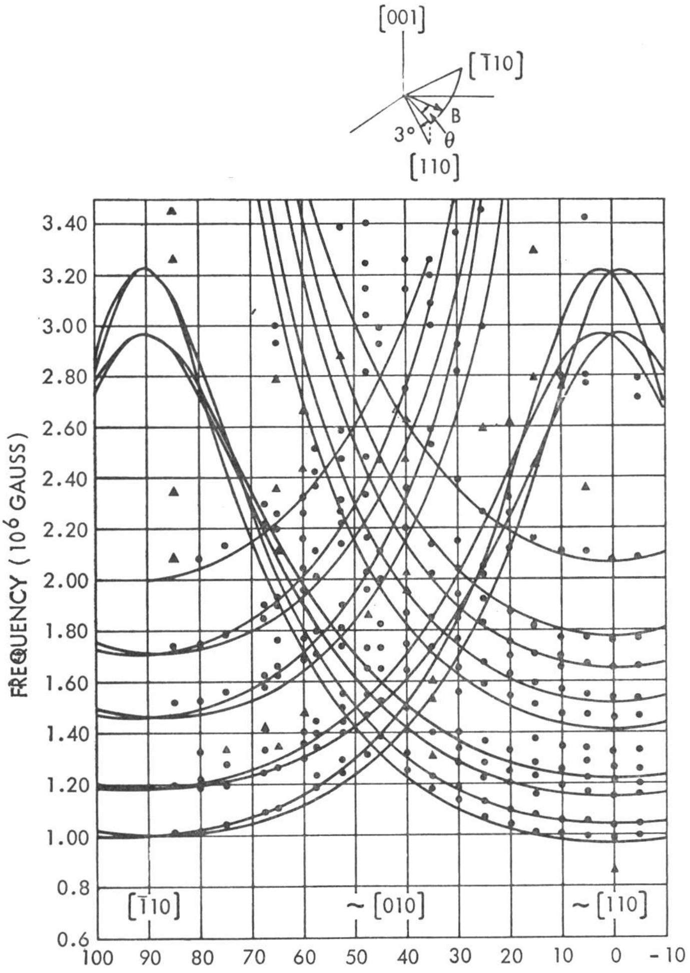

Fig. 5. Frequencies of the Shubnikov-de Haas oscillations versus the angle of rotation of the magnetic field B. B is rotated from approximately [110] to [$\bar{1}$10].

angle between the magnetic field and the major axis. The parameters p_s and K for each ellipsoid were determined by fitting eq. (2) to the data at [110] and [111]. The total number of carriers in four such ellipsoids already exceeds the total p determined from R_∞ by 70% without taking into account the other ellipsoids required by crystal symmetry. This result points to the existence of a single complicated surface with four extremal cross-sections.

For purposes of comparison with the data, eq. (2) was used to calculate all of the solid lines shown in Fig. 4. For the four curves minimizing at [111], the rate of increase of F for large values of $|\theta-35°|$ is greater than the calculated values and is more consistent with surfaces that are cylindrical rather than ellipsoidal in the region investigated. There also appears to be a splitting of the second to the lowest curve beginning at about 50 degrees, but we cannot establish that it is real.

The extremal cross-sections of the symmetrically related surfaces are observed only at those angles where these cross-sections are small. Thus even at this p, the extremal areas enclosed by the larger orbits cannot be measured with the present technique. Suppose however we assume that there are four surfaces located at the L-points and approximate each surface by a cylinder having a cross-section equal to the average of those observed at [111]. The largest cross-section of this cylinder would then correspond to a frequency of about 3.6×10^6 gauss.

Figure 5 shows the results obtained on Sample 670 when B was rotated in the (001) plane from [110] to [$\bar{1}$10]. Data on Sample 669 was also taken in this plane and the results are in excellent agreement. The angular variation of the frequencies in the ($\bar{1}$10) plane (Fig. 4) suggested that a 3 degree misalignment of the sample in the holder could produce the splitting of the curves that Fig. 5 exhibits. Using eq. (2) and introducing the 3 degree tilt shown in the diagram at the top of Fig. 5, we calculated the solid curves. The agreement with the data is reasonable enough to support our assumptions about misorientation. Notice that the splitting goes to zero in the [$\bar{1}$10] direction. This is because B is then perpendicular to the plane in which the misorientation can take place. Were it not for the splitting, the frequencies obtained at [110] would agree with those observed at [$\bar{1}$10]. They would also agree with those that are shown at [110] in Fig. 4. We see also that the curves cross at [010] as expected for a ⟨111⟩ model. The lack of points corresponding to the large frequencies that should be observed on each side of 45° is also evident.

According to the theory of the Shubnikov-de Haas effect,[10] harmonics of the fundamental frequency given by eq. (1) are considerably smaller in amplitude. However, for large spin splitting,[12] such as occurs in PbTe[13,14] for example, harmonics can predominate. Figure 3 shows that the line strength of the second harmonic of the fundamental frequency, 0.830 $\times10^6$ Gauss, is about twice that of the fundamental itself, and that the fourth harmonic is more prominent than the third. This situation prevails at all angles, as can be seen in Fig. 4. Thus a large g factor is associated with the carriers in the smallest section of the surface. This suggests that the band gap in SnTe is probably small.[15]

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DISCUSSION

Einspruch, N. G.: When you measured c_{44} of SnTe, did you measure the internal friction as well? Ordinarily, internal friction measurements are more sensitive to materials modifications than are sound velocity measurements.

Burke, J. R.: We found it very difficult to measure the internal friction because the attenuation was so small.

Esaki, L.: P. J. Stiles and I would like to make a proposal to explain interesting experimental results of Burke *et al.* because we feel it has some important ramifications for the direction of research in studying SnTe.

It is proposed that SnTe has its valence band maxima at the L points or near the L points on the Γ-L line. In any case the Fermi surface at $N=10^{20}$ holes/cm^3 is a surface of revolution, basically, a prolate ellipsoid of revolution, with its long axis parallel to the $\langle 111\rangle$ directions, as in PbTe ($k_F \sim (1+(K-1)\sin^2\theta)^{-1/2}$, where θ is the angle between k_F and the $\langle 111\rangle$ direction and $K=m_l/m_t$, the ratio of the longitudinal to transverse mass). However the surface is distorted (highly non-parabolic) such that the surface has bulges between its minimum k and maximum k($k_F \sim (1+(K-1)\sin^2\theta - b\sin^2 2\theta)^{-1/2}$, where $b>0$). It is distorted to such an extent, that there are now three extremal areas perpendicular to $k_{\langle 111\rangle}$ giving two identical maxima and one minima. This gives two Shubnikov-de Haas (SdH) frequencies which have their minimum frequency as a function of angle in the $\langle 111\rangle$ direction. It is implausible that there should be two valence band maxima unrelated by symmetry giving two sets of such ellipsoids to account for the four measured frequencies (which would require twice carrier density). To account for the number of carriers, and the extra frequencies which are observed, we are led to the following solution.

It has been assumed to date that SnTe is face-centered cubic (fcc) at 1 atm. at all temperatures. However it is proposed that the crystal structure changes from fcc to face-centered rhombohedral (fcr) [similar to GeTe at low temperatures] at some low temperature, which is still higher than the temperature at which the SdH data were taken. This suggestion is not unreasonable with the results of the transition point of the SnTe-GeTe alloy system work reported by Bierly, Muldawer and Beckman (Acta metallurgica **11** (1963) 447). An estimate of the distortion necessary to the model will be given later. The transition in the case of GeTe is very informative, at the transition temperature from fcc to fcr is 460°C for Ge saturated GeTe and 390°C for Te saturated GeTe. (L. E. Shelimova, N. Kh. Abrikosov and V. V. Zhdanova: Zhur. Neorg. Khim., tom X (1965) 1200). It is therefore conceivable that SnTe with $N=8\times10^{20}$/cm^3 would not transform whereas SnTe with $N=10^{20}$/cm^3 would, at say 30°K.

The most likely arrangement of the crystal after transforming is a separation into four sets of crystalites with the trigonal axis of each set parallel to one of the three-fold ($\langle 111\rangle$) axes of the fcc crystal. This type of distortion would tend to raise the band edge along the trigonal axis with respect to the other three. Therefore with the magnetic field along what one thought of as a fcc $\langle 111\rangle$, you would actually be looking along a fcr trigonal axis and obtain two SdH frequencies and also along three different fcr pseudo-trigonal axes and obtaining two more frequencies for a total of four which have their minimum value in the $\langle 111\rangle$ direction. This description does not take into account a change in the u parameter which might change the band gap and other parameters also, but it would still give four frequencies.

If one assumes that $K=11$, $b=1.4$ and scales the smaller two observed cross-sections in the $\langle 111\rangle$ direction to the pseudo-trigonal direction and the next smaller two to the trigonal direction, in their data for the $\{110\}$, the calculated volume contains 1.0×10^{20} holes/cm^3 versus 1.03×10^{20} holes/cm^3 measured by Burke *et al.* The angular variation is in good agreement except, and here is where a refinement of the model and data is necessary, the two frequencies for one surface should coalesce at 55° from the $\langle 111\rangle$ direction and this does not appear to happen for this choice of parameters. It is an important test of this model to find a coalescing point.

We may estimate the magnitude of the distortion from the deformation potential ($\sim 10^1$ v) the density of state mass ($0.3\, m_0$), and the separation of the frequencies in the $\langle 111 \rangle$ direction. This gives a value of $\Delta a/a \sim 10^{-3}$.

We are attempting to carry out an x-ray study at low temperatures as well as optical, tunneling and alloy studies to observe this phase transformation. So far we have a preliminary indication from tunneling that some sort of transformation takes place in some films between 10°K and 30°K.

Burke, J. R.: We considered the possibility of a phase change in SnTe. The elastic constants were measured as a function of temperature from 303°K to 1.3°K for a sample with a nominal carrier concentration of $8 \times 10^{20}\, \mathrm{cm}^{-3}$. However, the temperature variation was found to be quite smooth. Since the transition temperature for the phase change in GeTe is known to be carrier concentration dependent, we have recently looked for the phase change in a SnTe sample having a lower concentration of $2 \times 10^{20}\, \mathrm{cm}^{-3}$, close to the concentration of the samples on which we are reporting today, by measuring the temperature dependence of the strain in the $\langle 110 \rangle$ direction. No evidence for a phase change was found by this method which is sensitive to strains of the order of 10^{-6}. In addition, I would be surprised if our Shubnikov-de Haas oscillations would show so much structure in samples which had undergone a non-uniform phase change of the type suggested by Drs. Stiles and Esaki.