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Structural and Electrical Properties of TlBiTe_2 and TlTe^\dagger

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Samples of TlBiTe_2 and TlTe were prepared and characterized by x-ray powder diffraction, differential thermal analysis, scanning-electron-microscope and electron-microprobe studies, and transport measurements. The two materials were found to be distinctly different with regard to melting point, crystal structure, temperature dependence of the resistivity and Hall coefficient, and sign of the Hall coefficient and thermoelectric power. The Hall mobilities (in $\text{cm}^2/\text{V sec}$) are -64 and $+3$ at 300 K and -128 and $+1120$ at 4.2 K for TlBiTe_2 and TlTe , respectively. The temperature dependence of these mobilities, combined with the apparently large carrier densities, suggests that TlBiTe_2 is a highly degenerate n -type semiconductor, while TlTe is more likely to be a semimetal. Discontinuities in the resistivity and Hall-coefficient data of TlTe at 170 K suggest the occurrence of a phase change at that temperature. The two sets of results were compared with data on material which had been described by Hein and Swiggard as TlBiTe_2 , a new nonmetallic superconductor. But the normal-state properties of a portion of this material closely resemble those of TlTe , not TlBiTe_2 . A search for superconductivity in further samples of both compounds is needed to clarify this situation.

I. INTRODUCTION

Hein and Swiggard reported the discovery of superconductivity in the nonmetallic compound TlBiTe_2 .¹ The superconducting transition was broader in the larger of the two pieces on which the effect was studied, suggesting that the composition of the TlBiTe_2 ingot was not strictly homogeneous. A portion of the larger ingot was used to study the normal-state electrical properties of the compound.² These superconducting and normal-state studies will henceforth be identified as I and II.

The original purpose of the present work was to prepare additional samples of TlBiTe_2 and to carry out a more extensive investigation of its basic properties. It soon became clear, however, that the material studied in II more closely resembled TlTe rather than TlBiTe_2 .³ The revised goal of the work reported here then became the preparation and study of both compounds, with special emphasis on measurements that would clearly distinguish one from another.

Since Tl and Bi immediately precede and follow Pb in the periodic table, TlBiTe_2 may be regarded as "pseudo-PbTe." This heightens the interest in

establishing firmly the superconducting properties of TlBiTe_2 , since there has been a controversy of nearly 40 years duration, still not completely settled, as to whether the lead chalcogenides PbTe, PbSe, and PbS can, under any circumstances, become superconducting.

The literature on TlBiTe_2 is rather meager. As far as we know, none of its properties had been studied below room temperature until the work reported in I and II was carried out. Its preparation was described by Bither in his patent.⁴ Hockings and White determined its melting point to be 535°C and found that its structure was a rhombohedral distortion of the NaCl lattice,⁵ ordered in the sense that successive layers normal to the trigonal axis occur in the sequence $-\text{Tl}-\text{Te}-\text{Bi}-\text{Te}-$.

Originally, there had been disagreement as to whether the ternary compound which formed in the Tl-Bi-Te system was TlBiTe_3 (Ref. 6) or TlBiTe_2 (Ref. 7). The transport data thus far reported for TlBiTe_2 have been puzzling. Mazelsky and Lubell measured a room-temperature value of $-70\ \mu\text{V}/\text{K}$ for the thermoelectric power, but a positive weak-field Hall coefficient (R_0) in the range $0.30-0.35\ \text{cm}^3/\text{C}$.⁸ The Hall data suggest a nominal carrier density (i. e., that given by $1/R_0 e$) $p^* \approx 2 \times 10^{19}\ \text{cm}^{-3}$.

On the other hand, Akhmedova *et al.*⁹ found a smaller and negative R_0 at room temperature, corresponding to $n^* \approx 2 \times 10^{20} \text{ cm}^{-3}$. Furthermore, they reported the unusual result that both R_0 and the resistivity ρ ($= 1 \times 10^{-3} \Omega \text{ cm}$) were essentially temperature independent between 300 and 500 K. The room-temperature Hall mobility ($\mu_H = R/\rho$) was about $25 \text{ cm}^2/\text{V sec}$.

The compound TlBiTe_2 also deserves attention as a member of an interesting family of materials of the type Tl-V-VI_2 ($V = \text{As, Sb, or Bi}$; $\text{VI} = \text{S, Se, or Te}$). An unusually wide variety of crystal structures is found among this group of nine compounds.¹⁰ Some of them may also be prepared in amorphous form¹¹; in that state they exhibit the type of non-destructive switching and memory behavior that has attracted so much attention recently.¹²

There is a fairly extensive literature on the several intermediate phases of the Tl-Te system, which include Tl_2Te_3 , TlTe , Tl_5Te_3 , Tl_3Te_2 , and Tl_2Te . The existence of the last two has been disputed. But the information on TlTe , as in the case of TlBiTe_2 , is rather scanty. Rabenau *et al.* found that it forms peritectically at 300°C , in a body-centered tetragonal structure.¹³ They reported a room-temperature thermoelectric power of $+50 \mu\text{V/K}$, but mentioned no other transport data.

Flicker and Grass studied the electrical resistivity between 77 K and room temperature.¹⁴ They found a negative temperature coefficient above about 150 K, and concluded that TlTe was a semiconductor with an energy gap of 0.15 eV. The room-temperature value of ρ was about $0.5 \Omega \text{ cm}$.

Cruceanu and Slădaru, on the other hand, measured ρ between 77 and 550 K and found it to increase with increasing temperature.¹⁵ The room-temperature value was only about $5 \times 10^{-4} \Omega \text{ cm}$. They reported a temperature-independent positive Hall coefficient of less than $10^{-3} \text{ cm}^3/\text{C}$ ($p^* \geq 6 \times 10^{24} \text{ cm}^{-3}$), hence a room-temperature Hall mobility less than $2 \text{ cm}^2/\text{V sec}$. They also found a positive thermoelectric power which was directly proportional to temperature and had reached a value of about $15 \mu\text{V/K}$ at room temperature. In addition, they confirmed the crystal structure reported earlier by Rabenau *et al.*¹³

We also want to note that Tl_5Te_3 has been found to become superconducting at 2.19 K .¹⁶

II. EXPERIMENT

The TlBiTe_2 and TlTe samples were prepared from commercially available 99.9999% pure elements. The appropriate amounts of the elements were sealed in Vycor glass ampoules at a vacuum of less than 10^{-6} Torr .

The TlBiTe_2 samples were grown using a modified Bridgman technique. The samples were heated to 650°C and maintained at that temperature for

several hours with periodic agitation to ensure thorough mixing of the constituents. In the conventional Bridgman technique, the ampoule is lowered mechanically through a temperature gradient at a constant rate. In our method, the constant-temperature gradient of 10°C/in. was passed over the stationary ampoule electronically at a rate of 4°C/h. The lower end of the ampoule was tapered in order to favor crystal growth at a single point.

The TlTe samples were prepared by a different method since this compound forms by a peritectic reaction. The appropriate composition was sealed off as before, held at 500°C for several hours with occasional agitation, and then quenched in water. The resulting ingot was next reheated to 300°C , held at this temperature for 3 days, and again quenched in water.

Rectangular bars approximately $1 \times 2 \times 6 \text{ mm}$ were cut from ingots of the two materials by the usual cutting and lapping techniques. A visual examination of the TlBiTe_2 samples after lapping showed clearly that the material was not single phase. A bright second phase was present as small inclusions in a gray matrix. This minor phase constituted approximately 10% of the surface area. The TlTe samples did not show any obvious phase separation or heterogeneity at room temperature after shaping into Hall samples. However, as the TlTe was heated in air the oxidation rate was clearly not uniform over the entire surface area. In addition, a second phase could be seen bubbling out of the material well below the melting point of TlTe .

A Debye-Scherrer powder pattern was taken for each ingot and crystal grown during this study. The powder (particle size: $44\text{--}74 \mu\text{m}$) was annealed for several days to relieve strains induced by grinding. Overnight exposures generally produced easily resolvable lines.

A differential-thermal-analysis (DTA) apparatus¹⁷ was designed and constructed to provide an additional way to check on the structural nature of the material. The DTA samples were prepared from the same slice of ingot or crystal as were the Hall and x-ray specimens.

The scanning-electron-microscope¹⁸ and electron-microprobe¹⁹ studies were performed on slices adjacent to those used for the DTA, Hall, and x-ray samples. These studies yielded the most definitive information as to the structural character of the material used in this investigation. The chemical compositions could be determined to an accuracy of $\frac{1}{2} \text{ at. } \%$ by the electron microprobe.

The electrical properties were measured using the standard dc potentiometric techniques. Electrical contacts to TlBiTe_2 consisted of 0.002-in. copper wires which were attached by soldering. Leads to TlTe were very difficult to solder and were finally made with 0.002-in. platinum wires

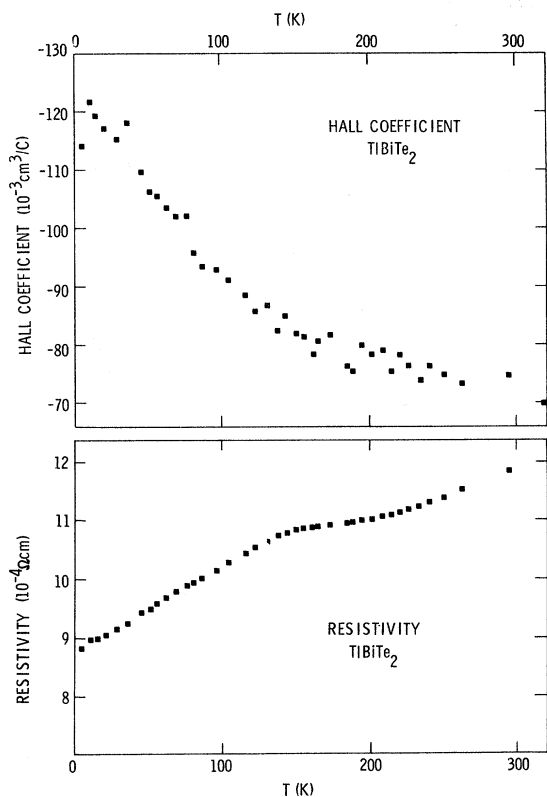


FIG. 1. Resistivity and weak-field Hall coefficient as a function of temperature between 300 and 4.2 K for our TlBiTe_2 .

attached by capacitive discharge. Temperature-dependent electrical measurements were performed in a variable-temperature gas-exchange Dewar in which the temperature was stabilized to 0.01 K by a Cryogenic Research controller with platinum or germanium sensors.

The sign of the thermoelectric power was determined with a simple thermal-probe test set.

III. RESULTS AND DISCUSSION

A. Electrical Properties of TlBiTe_2

As mentioned above, the crystals of TlBiTe_2 showed clear evidence of phase separation after the cutting and grinding step in the preparation of Hall samples. Electrical measurements were made on those samples which had the least amount ($\sim 10\%$) of this minor phase. (The multiphase nature of TlBiTe_2 will be discussed in more detail in Sec. III B.) The resistivity ρ and the weak-field Hall coefficient R_0 were measured between 300 and 4.2 K. These results are shown in Fig. 1 for one TlBiTe_2 sample. A second sample had essentially the same properties. Figure 2 contains the corresponding results for the samples studied in II (hereafter called the NRL material). It is imme-

diately evident that the two sets of measurements differ greatly from each other. One of the most prominent features of the earlier data was the abrupt increases at 170 K in ρ and R_0 (by factors of 1.2 and 3, respectively) with cooling. No such structure is present in the Hall data in Fig. 1. Although the resistivity curve in that figure exhibits a change of slope near 150 K, its magnitude does not change abruptly as do the earlier results in Fig. 2.

Other important differences are summarized in the first two lines of Table I: opposite signs for the weak-field Hall coefficient R_0 and thermoelec-

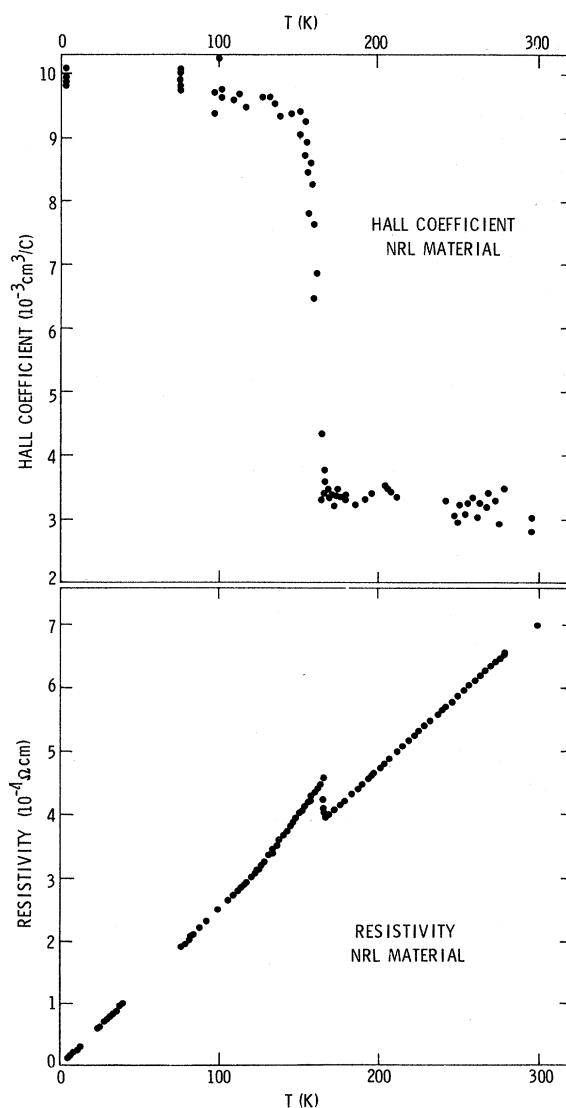


FIG. 2. Resistivity and weak-field Hall coefficient as a function of temperature between 300 and 4.2 K for the NRL material.

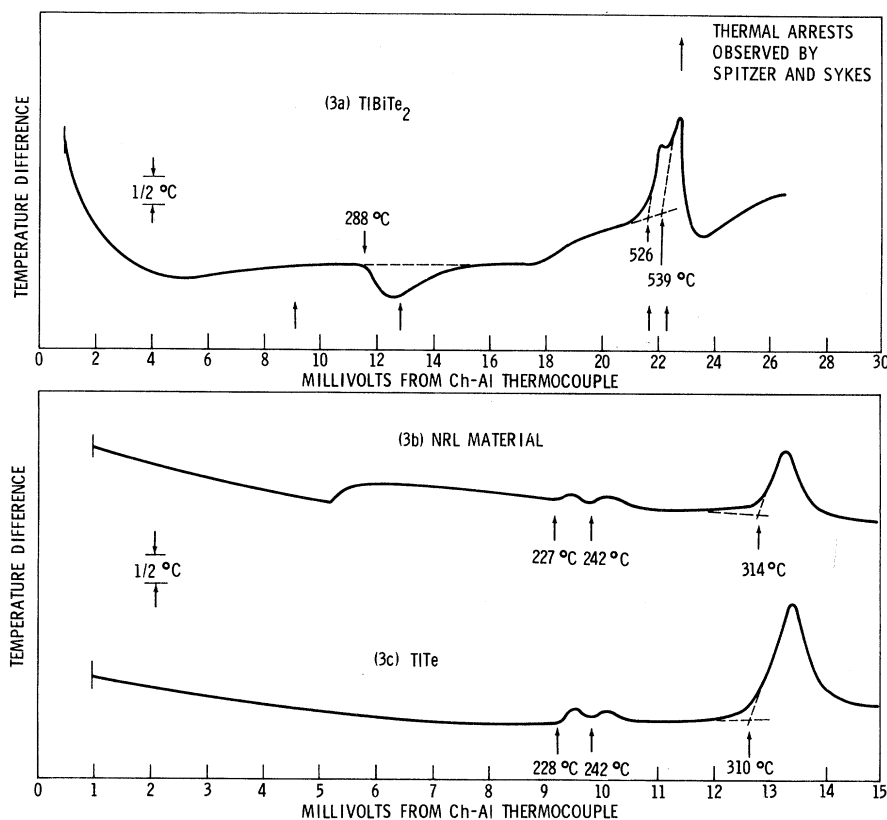


FIG. 3. Differential thermal analysis for (a) TlBiTe_2 , (b) NRL material, and (c) TlTe . X axis measures the output of a chromel-alumel thermocouple. Arrows in (a) indicate thermal arrests observed by Spitzer and Sykes (Ref. 6).

tric power, a factor-of-10 difference in the magnitude of R_0 , and a Hall mobility for our TlBiTe_2 which is much higher at room temperature and much lower at 4.2 K than the corresponding values for the NRL material.

B. Structural Analysis of TlBiTe_2 and the NRL Material

Because of the striking differences enumerated above, we carried out a thorough materials analysis of our TlBiTe_2 samples and the portion of the NRL ingot on which the electrical measurements had been made.

The first observation was that the NRL material melted at $(310 \pm 10)^\circ\text{C}$, much below the melting point of TlBiTe_2 at $(540 \pm 5)^\circ\text{C}$.^{4,5} A second phase was seen bubbling out of the NRL samples at

232°C .

Figure 3(a) presents a DTA recording of the ingot from which our TlBiTe_2 crystals were prepared. The first unbalance in the heating curve occurs at 288°C , with a well-defined double peak at higher temperatures. By extrapolating base lines and line profiles as shown in Fig. 3(a), we conclude that thermal arrests associated with the double peak occurred at 526 and 539°C . This is in excellent agreement with Spitzer and Sykes⁷ who observed the thermal arrests indicated by arrows just below the heating curve. The 539°C thermal arrest agrees very well with the reported melting point of TlBiTe_2 . The lower peak in the doublet corresponds, according to Spitzer and Sykes, to a eutectic. They ascribe two additional thermal arrests

TABLE I. Electrical properties.

Material	Hall coefficient ($10^{-3} \text{ cm}^3/\text{C}$)		Carrier concentration ^a (10^{20} cm^{-3})		Hall mobility ($\text{cm}^2/\text{V sec}$)		Sign of thermoelectric power
	300 K	4.2 K	300 K	4.2 K	300 K	4.2 K	
TlBiTe_2	-76	-125	0.82	0.50	-64	-128	-
NRL material	+3.0	+10.0	20.8	6.2	+4	+1200	+
TlTe	+2.6	+7.5	24.0	8.3	+3	+1120	+

^aDerived from the formula $1/eR_0$.

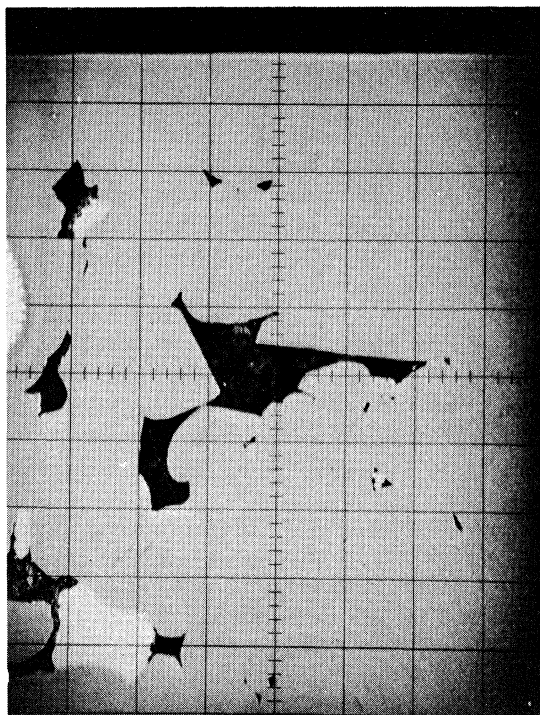


FIG. 4. Target-current photograph of TlBiTe_2 taken during electron-microprobe study. See Table II for identification of various phases.

at 315 and 224 °C to inclusions of TlTe and Tl_2Te_3 , respectively. We were unable to associate the exothermic arrest at 288 °C in our DTA heating curve with any feature of the Bi-Te or Tl-Te phase diagrams. Figure 3(b) shows the DTA curve for the NRL material. No thermal arrests were observed above 314 °C.

Next, the materials were examined with a scanning electron microscope (SEM).¹⁸ No bismuth was detected in the NRL samples. Although the instrument was not calibrated for quantitative analysis, we were able to conclude that no more than about 2 at. % bismuth was present. Thus, the NRL material was definitely not TlBiTe_2 . The SEM analysis of our TlBiTe_2 samples also revealed that they contained three phases. The major phase ($\approx 80\%$ by volume) showed the following number of counts (using a 100-sec counting interval): 425, 360, and 1780 for the elements Tl, Bi, and Te, respectively. The corresponding counts for the first minor phase ($\approx 15\%$) which forms at the grain boundaries of the major phase are 735, 0, and 2135. The second minor phase ($\approx 5\%$), which forms a eutectic with the first minor phase, appears to be elemental tellurium. Under the optical microscope the typical light-dark regions characteristic of eutectic formation are observed at some of the grain boundaries.

The electron-microprobe analysis¹⁹ made it possible to determine the chemical composition of the various phases to within about $\frac{1}{2}$ at. %. It showed, first of all, that the major phase of our TlBiTe_2 ($\approx 80\%$ by volume) was the ternary compound with that formula, agreeing with Spitzer and Sykes⁷ and disagreeing with Borisova *et al.*⁶ who asserted that the compound was TlBiTe_3 . Figure 4 shows a target-current photograph of our TlBiTe_2 crystal taken during the microprobe investigation. The large gray matrix was identified as TlBiTe_2 while the light gray and dark regions are the minor phases.

The microprobe confirmed that the NRL material was devoid of bismuth and identified the major phase as TlTe with a minor phase ($\approx 5\%$ by volume) of elemental tellurium. A target-current photograph of the NRL material is shown in Fig. 5. The gray matrix and dark areas are TlTe and Te, respectively. The gray, fuzzed areas in Fig. 5 are smudges which could not be avoided in the surface preparation.

The usefulness of the x-ray studies was somewhat hampered by the multicomponent nature of the specimens. In the case of TlBiTe_2 we obtained fair agreement with the indexing associated with the rhombohedral-unit-cell dimensions reported by Hockings and White.⁵ We also found extra d spacings which could not be fitted to their indexing

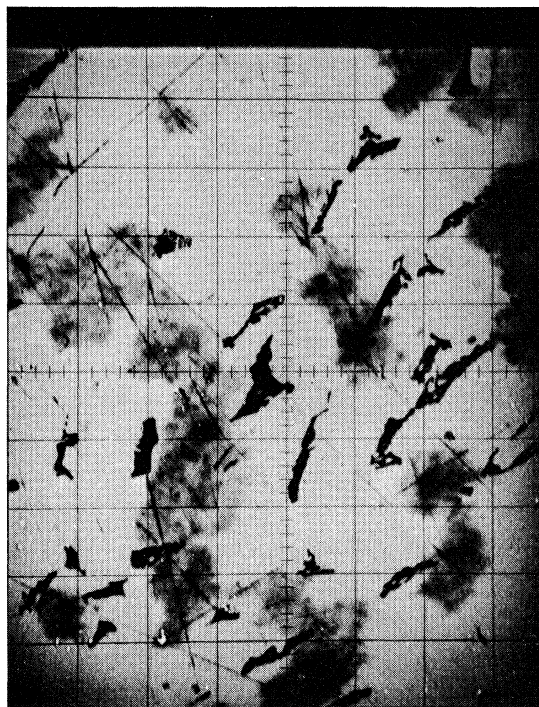


FIG. 5. Target-current photograph of NRL material taken during electron-microprobe study. See Table II for identification of phases.

scheme. These were presumably due to the presence of the minor phases.

The d spacings obtained for the NRL material were completely unrelated to the structure given by Hockings and White for TlBiTe_2 , but were in excellent agreement with the interatomic spacings reported by Cruceanu and Slădaru¹⁵ for TlTe .

The results of the x-ray-diffraction, DTA, SEM, and the electron-microprobe studies of our TlBiTe_2 and the NRL material are summarized in the first two lines of Table II.

C. Preparation and Properties of TlTe

After learning that the portion of the NRL material studied in II was TlTe , not TlBiTe_2 , we decided to prepare crystalline TlTe and investigate its compositional and electrical properties. The corresponding material-analysis data on TlTe are given in line three of Table II and in Fig. 6. The d spacings obtained by x-ray powder diffraction were in excellent agreement with the interatomic spacings reported by Cruceanu and Slădaru¹⁵ for TlTe .

The DTA and electron-microprobe analyses showed that our original ingot of TlTe contained several phases which are identified in Table II (later samples were almost entirely TlTe). The mottled light-dark areas shown in Fig. 6(b) are characteristic of eutectic formation. The ill-defined dark areas are again smudges formed during the surface preparation.

Figure 7 presents ρ and R_0 as a function of temperature from 300 to 4.2 K for two polycrystalline TlTe samples; for comparison, the data on the NRL material studied in II are shown as dashed lines. The over-all agreement between the two

sets of data is very good, taking into account the fact that the samples were noncubic, polycrystalline, and not entirely single phase. As already mentioned in II, the kinks in the transport data suggest that a phase change occurs at 170 K. Unfortunately, our present equipment will not permit us to carry out x-ray studies below this temperature. The nature of the low-temperature phase is of particular interest because of its relevance to the occurrence of superconductivity.

The third line of Table I summarizes the electrical and thermoelectric properties of our TlTe . It is evident that they closely resemble the corresponding data for the NRL material but are very different from those for TlBiTe_2 .

IV. CONCLUDING REMARKS

This paper has described our efforts to obtain more definitive data on the basic properties of two compounds TlBiTe_2 and TlTe . The results were not completely satisfactory, because in both cases we were not able to prepare single-crystal or entirely single-phase material.

We were able to demonstrate that the chemical compositions of the major phases of our two types of material did correspond accurately to the formulas TlBiTe_2 and TlTe and had the crystal structures (rhombohedral and tetragonal) and the melting points (approximately 535 and 300 °C) previously reported for them.

Since our electrical measurements were made on polycrystalline noncubic material, they represent average values; furthermore, they may have been significantly affected by the presence of the minor phases. Fortunately, however, the results in both cases do agree reasonably well with previously

TABLE II. Analysis of materials.

MATERIAL	X-RAY DIFFRACTION	DTA ARRESTS	SCANNING ELECTRON MICROSCOPE = 100 SEC COUNT ^a				ELECTRON MICROPROBE ^b				
			Relative Amount	Number of Counts			Photograph	Relative Amount	Atomic Per Cent		
				Tl	Bi	Te			Tl	Bi	Te
TlBiTe_2	Fair agreement with Ref. 5 on TlBiTe_2	288°C	80% ^c	425	360	1780	Gray Matrix ^e	80% ^c	24.5	28.3	50.0
		526	15	735	0	2100	Dark Areas ^e	15	26.0	0.4	73.6
		539	5	0	0	7500	Light Areas ^e	5	53.5	8.6	38.8
NRL MATERIAL	No agreement with Ref. 5 on TlBiTe_2	227	—	—	0 ^d	—	Gray Matrix ^f	85	50.3	0.0	50.6
		242 314	—	—	—	—	Dark Areas ^f	15	0.2	0.0	99.8
TlTe	Excellent agreement with Ref. 15 on TlTe	232	NOT ANALYSED BY SEM				Gray Matrix ^g	65	50.5	0.0	50.1
		242					Light Area ^g	10	62.9	0.0	37.7
		308					Light Dark) eutectic ^g	25	46.6 17.3	0.0 0.0	54.1 82.6

^aReference 18.

^cApproximate relative volume.

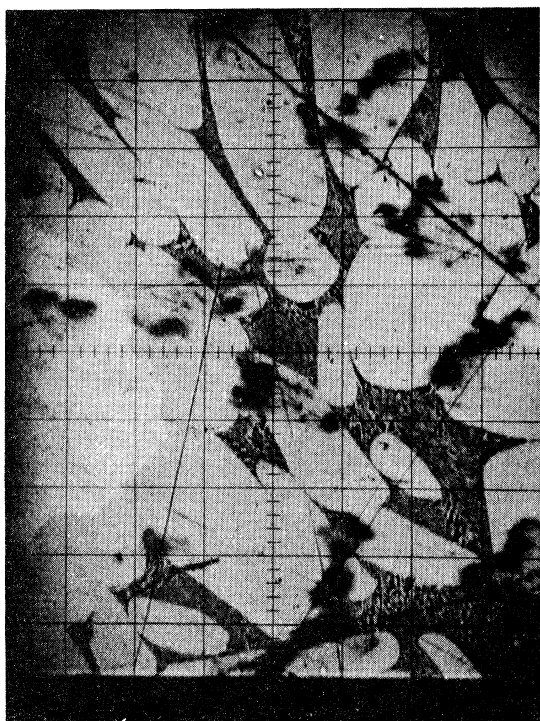
^eSee Fig. 4.

^fSee Fig. 6.

^bReference 19.

^dAnalyzed for bismuth only.

^fSee Fig. 5.



(a)



(b)

FIG. 6. (a) Target-current photograph of TlTe taken during electron-microprobe study at 200X; (b) same as (a) but at 500X, showing more clearly the mottled light-dark eutectic phase. See Table II for identification of phases.

published data.

Our Hall and thermoelectric data, the Hall data of Akhmedova *et al.*,⁹ and the thermoelectric data of Mazelsky and Lubell⁸ all suggest that as-grown TlBiTe_2 is *n* type. Now that we have discovered that the NRL material studied in II was not TlBiTe_2 , the only sign discrepancy thus far reported is the positive room-temperature Hall coefficient found by Mazelsky and Lubell.⁸

The temperature dependences of our TlBiTe_2 Hall and resistivity data between 4.2 and 300 K are consistent with the constant values found by Akhmedova *et al.* between 300 and 500 K.⁹ Although our Hall coefficient is noticeably temperature dependent below 100 K, that dependence becomes weaker with increasing temperature and has essentially vanished at room temperature.

The resistivity data for our TlBiTe_2 material exhibit an unusually shallow temperature dependence; the over-all decrease between 300 and 4.2 K amounts to only about 25%. This behavior is characteristic of a highly disordered, extrinsic semiconductor. Of course, it might also be a semi-metal, but the lack of any temperature variation in the Hall coefficient between 300 and 500 K argues against this interpretation.

The magnitudes of the room-temperature resistivity obtained by us and by Akhmedova *et al.* agree to within about 10%. The corresponding Hall-coefficient values differ by a factor of $2\frac{1}{2}$. For the present, we do not regard this as a serious discrepancy, taking into account the small magnitudes of R_0 and the extreme sensitivity of this parameter to the imperfect nature of the samples. Furthermore, Akhmedova *et al.* assert, as we do not, that their material was single phase; this circumstance alone could easily account for the difference between the two results.

Since the resistivities are essentially equal, our room-temperature Hall mobility for TlBiTe_2 is some $2\frac{1}{2}$ times higher than that obtained by Akhmedova *et al.* This situation is reminiscent of that found in high-carrier-concentration samples of PbTe and SnTe . In those cases, a mobility which is inversely proportional to carrier density is generally believed to reflect the highly nonparabolic nature of the bands in the two compounds.

So far as we know, all measurements of the Hall coefficient and thermoelectric power thus far reported for TlTe have been positive, and all except one¹⁴ have indicated extrinsic rather than intrinsic semiconducting behavior.¹³⁻¹⁵

The present results, as did those in II, suggest that a phase change takes place in TlTe at 170 K. However, there is no suggestion of any kink in the TlTe resistivity-vs-temperature data published by Cruceanu and Slădaru.¹⁵ We can only speculate that the presence of other phases in their samples may

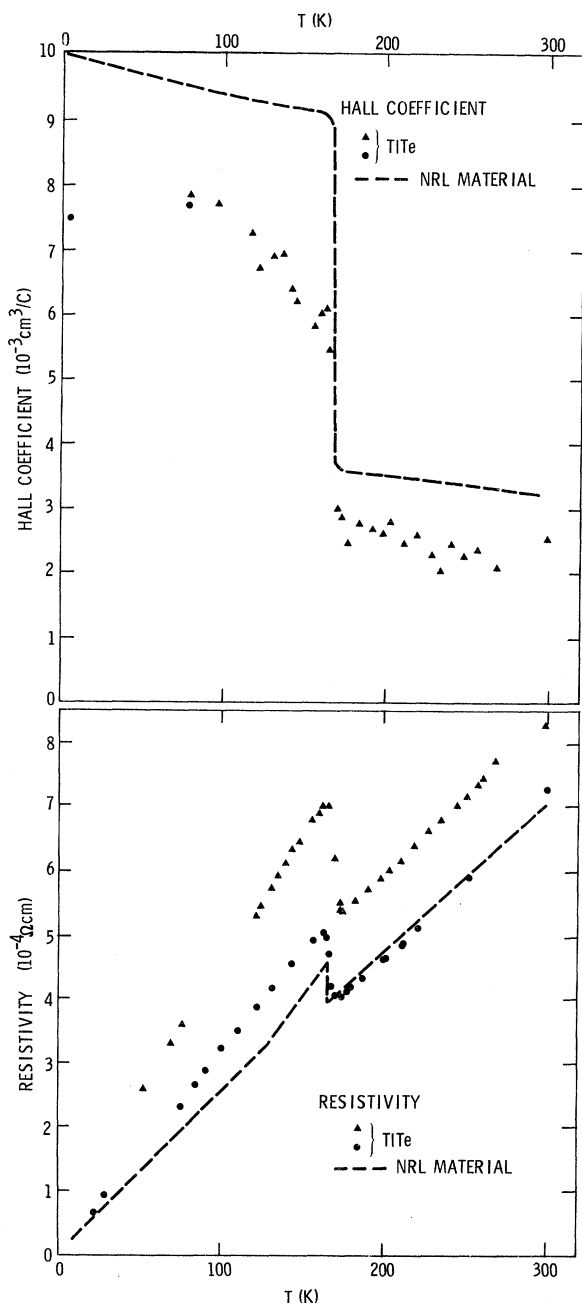


FIG. 7. Resistivity and weak-field Hall coefficient as a function of temperature between 300 and 4.2 K for two TlTe samples. The data on the NRL samples are dashed in for comparison.

have inhibited the occurrence or the detection of the phase change.

We should note that Cruceanu and Slădaru's resistivity data for both TlTe and Tl_5Te_3 gradually level off and become essentially constant above about 500 K. We saw no such tendency up to 300 K in our TlTe resistivity data, nor did Juodakis and Kannewurf, up to 500 K, in their resistivity mea-

surements on Tl_5Te_3 .¹⁶

The present resistivity data on TlTe, as well as those reported in II, are two orders of magnitude smaller at 4.2 than at 300 K, and show little or no sign of leveling off. This is in sharp contrast to the shallow temperature dependence found in TlBiTe_2 . As noted in II, the estimated defect-scattering cross section per scattering center in TlTe is $0.1 \text{ } \text{Å}^2$.

From the semiconductor point of view, this is an upper limit, obtained by assuming that the number of scatterers is no larger than the number of extrinsic carriers. The simplest way to avoid this unreasonably small cross section is to conclude that TlTe is a semimetal. Then it may be assumed that the number of scatterers is much smaller than the carrier density, and hence the scattering cross section per scatterer becomes much larger.

The room-temperature values of ρ in the present work, in II, and in the data of Cruceanu and Slădaru all lie in the range $5\text{--}8 \times 10^{-4} \text{ } \Omega \cdot \text{cm}$. There is one discrepancy: Flicker and Grass found that ρ was much larger and had a negative temperature coefficient. These characteristics much more closely resemble those of the intrinsic semiconductor Tl_2Te_3 .¹⁵

The room-temperature Hall mobility in our TlTe is very low, only $3\text{--}4 \text{ cm}^2/\text{V sec}$. This is reasonably consistent with the upper limit of $2 \text{ cm}^2/\text{V sec}$ found by Cruceanu and Slădaru.¹⁵ Of course, if this compound is a semimetal, the mobilities of the electrons, or holes, or both, must be higher than these values.

In summary, we have measured several basic properties of TlBiTe_2 and TlTe. We have confirmed their crystal structures and melting points. The present work and that in II extended the Hall-coefficient and resistivity measurements to lower temperatures than previously reported. The results agreed rather well with most of the earlier measurements.

The transport characteristics of the two compounds are distinctly different in three respects: TlBiTe_2 is n type, its resistivity is a very weak function of temperature, and its resistivity and Hall coefficient are smooth functions of temperature; TlTe is p type, its resistivity is a strong function of temperature, and its resistivity and Hall coefficient exhibit sharp kinks, suggesting a phase change, at 170 K.

This paper has also shown that a portion of material prepared at the Naval Research Laboratory, which was previously thought to be TlBiTe_2 , was actually TlTe. We are presently initiating a collaborative study with R. A. Hein, who will search for superconductivity in well-characterized samples of both compounds. We expect to find out shortly which one is actually the superconductor.

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¹R. A. Hein and E. M. Swiggard, *Phys. Rev. Letters* **24**, 53 (1970).

²R. S. Allgaier, R. Perl, and E. M. Swiggard, in *Physics of Semimetals and Narrow-Gap Semiconductors*, edited by D. L. Carter and R. T. Bate (Pergamon, New York, 1971), p. 437.

³A partial report was presented earlier by J. D. Jensen, D. W. Ernst, J. R. Burke, and R. S. Allgaier [*Bull. Am. Phys. Soc.* **16**, 652 (1971)].

⁴T. A. Bither, Jr., U. S. Patent No. 2, 893, 831, July 7, 1959.

⁵E. F. Hockings and J. G. White, *Acta Cryst.* **14**, 328 (1961).

⁶L. A. Borisova, M. V. Efremova, and V. V. Vlasov, *Dokl. Akad. Nauk SSSR* **149**, 117 (1963) [*Sov. Phys. Doklady* **149**, 196 (1963)].

⁷D. P. Spitzer and J. A. Sykes, *J. Appl. Phys.* **37**, 1563 (1966).

⁸R. Mazelsky and M. S. Lubell, *J. Phys. Chem.* **66**, 1408 (1962).

⁹F. I. Akhmedova, I. G. Sorokina, and R. S. Giniyatulin, *Izv. Vyssh. Ucheb. Zaved. Fiz.* **11**, No. 11, 138 (1968).

¹⁰See Ref. 2 for a listing and further references.

¹¹For a review of earlier work, see B. T. Kolomiets, *Phys. Status Solidi* **7**, 359 (1964); **7**, 713 (1964).

¹²See pertinent papers in *J. Non-Cryst. Sol.* **2** (1970); **4** (1970).

¹³A. Rabenau, A. Stegherr, and P. Eckerlin, *Z. Metallk.* **51** (1960).

¹⁴P. Flicker and F. Grass, *Z. Metallk.* **57**, 641 (1966).

¹⁵E. Cruceanu and St. Slădaru, *J. Mater. Sci.* **4**, 410 (1969).

¹⁶A. Juodakis and C. R. Kannewurf, *J. Appl. Phys.* **39**, 3003 (1968).

¹⁷J. D. Jensen and D. W. Ernst (unpublished).

¹⁸This analysis was performed by J. Jellison of the Materials Engineering Branch of the National Aeronautics and Space Administration, Goddard Space Flight Center, Greenbelt, Md.

¹⁹This analysis was performed by R. L. Myklebust and C. E. Fiori of the Spectrochemical Analysis Section, National Bureau of Standards, Gaithersburg, Md.

Temperature Dependence of Alfvén-Wave Amplitudes and Carrier Relaxation Times in Bismuth

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Alfvén-wave propagation in parallel-plate Bi samples has been studied using a 24-GHz microwave reflection spectrometer. The attenuation of Alfvén-wave amplitudes in a magnetic field up to 10 kG was measured at different temperatures ranging from 2.4 to 11°K. From the amplitude of the weakly damped waves, effective relaxation times of charge carriers were measured directly without using any band-structure parameter. The temperature dependence of the effective relaxation times can be fitted to a T^{-2} variation with different slopes for different crystal orientations.

I. INTRODUCTION

The propagation of low-frequency electromagnetic waves in solid-state plasmas has been the subject of many recent investigations.¹ In the presence of a dc magnetic field, waves can propagate in metals and semiconductors with little attenuation when the wave frequency ω is much lower than the cyclotron frequency ω_c of the charge carriers in the solid which can be regarded as a stable plasma. Various modes of wave propagation have been extensively investigated in several laboratories. If the solid contains equal numbers of electrons and holes, as in Bi and other group-V semimetals, the magnetoplasma wave propagates in a linearly polarized mode, known as the Alfvén

wave.

In the Alfvén mode, the propagation vector of the wave is determined by the diagonal magnetoresistance term in the conductivity tensor. As a result, the power absorption in the solid-state plasma is directly proportional to the dc magnetic field H and the wave is heavily damped except for $\omega\tau \gg 1$ (τ is the carrier relaxation time). However, when the conditions for Alfvén-wave propagation are satisfied, measurements of the wave characteristics can be used in complement with the ordinary magnetoresistance studies to obtain information on the electronic structure of the solids.

To date, Alfvén waves have been used to study the carrier concentration and effective masses of electrons and holes in Bi. More recently, from

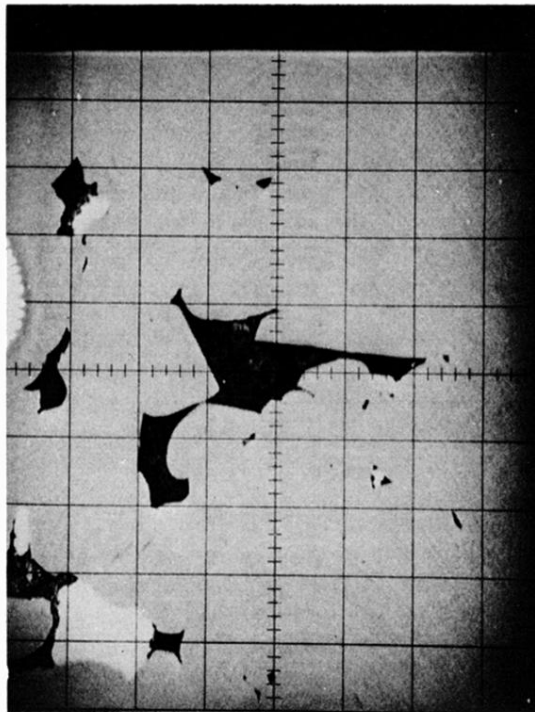


FIG. 4. Target-current photograph of TlBiTe₂ taken during electron-microprobe study. See Table II for identification of various phases.

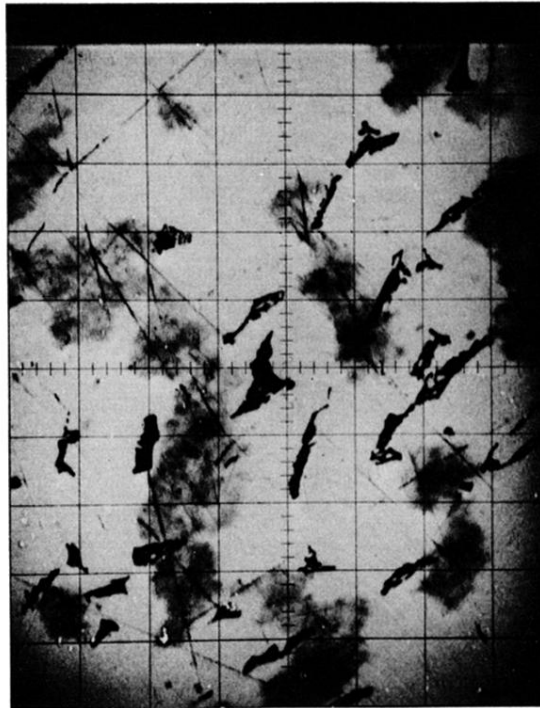
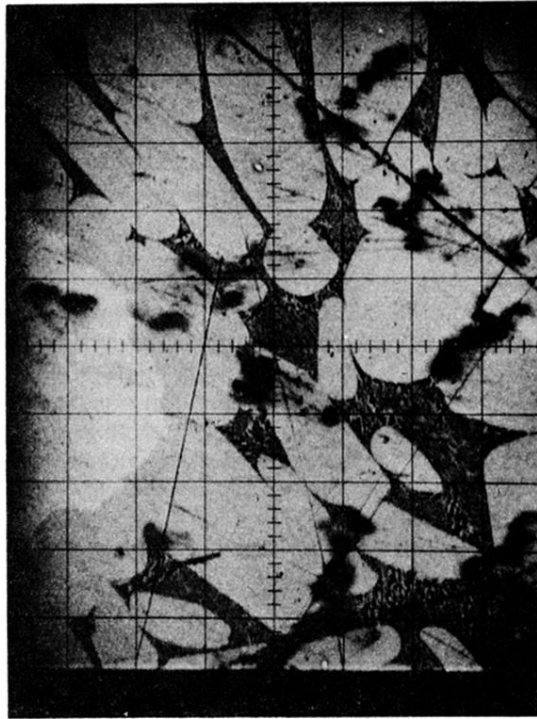


FIG. 5. Target-current photograph of NRL material taken during electron-microprobe study. See Table II for identification of phases.



(a)



(b)

FIG. 6. (a) Target-current photograph of T1Te taken during electron-microprobe study at 200X; (b) same as (a) but at 500X, showing more clearly the mottled light-dark eutectic phase. See Table II for identification of phases.