

THE PHASE DIAGRAM FOR THE BINARY SYSTEM INDIUM–TELLURIUM AND ELECTRICAL PROPERTIES OF In_3Te_5 *

EDWARD G. GROCHOWSKI,† DONALD R. MASON, GERALD A. SCHMITT
and PHILLIP H. SMITH‡

The Department of Chemical and Metallurgical Engineering, The University of Michigan
Ann Arbor, Michigan

(Received 22 October 1963; revised 13 December 1963)

Abstract—The phase diagram for the binary system indium–tellurium has been clarified and corrected, particularly in the region near the composition In_2Te_3 . This material is a potentially important semiconductor, either alone or in combination with other materials, such as Cu_3Te , Ag_2Te , CdTe , etc.

Results of this study were obtained by correlating differential thermal analysis (DTA), chemical analyses of zone-refined ingots, microscopic analysis, and X-ray determinations.

Two new phases have been identified, and the compositions of three other phases have been determined more precisely.

(1) The phase In_2Te (33.3 at. % Te) does not exist; the composition should be In_9Te_7 (43 at. % Te). The peritectic decomposition temperature is 462°C .

(2) The phase InTe (50.0 at. % Te) has the composition $\text{In}_{30}\text{Te}_{31}$ (50.8 at. % Te). The congruent melting point is 696°C .

(3) A new phase In_3Te_4 (57.0 at. % Te) has been found having a peritectic decomposition temperature of 650°C .

(4) The phase In_2Te_3 (60.0 at. % Te) has the composition $\text{In}_{27}\text{Te}_{40}$ (59.7 at. % Te). The congruent melting point is 667°C , and there is a phase transition at about 550°C .

(5) A new phase In_3Te_5 (62.5 at. % Te) has been found, having a peritectic decomposition temperature of 625°C , and a phase transition at 463°C .

(6) The phase In_2Te_5 (71.5 at. % Te) was prepared.

(7) Electrical measurements on In_3Te_5 show a large conductivity increase associated with the phase transition at 463°C .

(8) Electrical measurements on zone refined In_2Te_3 , were non-reproducible.

1. INTRODUCTION

BECAUSE of the potential importance of compounds in a binary system indium–tellurium^(1,2) as semiconductor materials, a re-investigation of this phase diagram has been undertaken to clarify and correct certain discrepancies in the published literature. This report is an extension of comments

which were made in Prague in discussing a paper by ZHUZE, *et al.*⁽³⁾ Experimental results from differential thermal analysis data, microscopic analyses, electrical measurements and chemical analyses of zone-refined ingots have been correlated with data from the literature in arriving at the phase diagram presented in this paper.

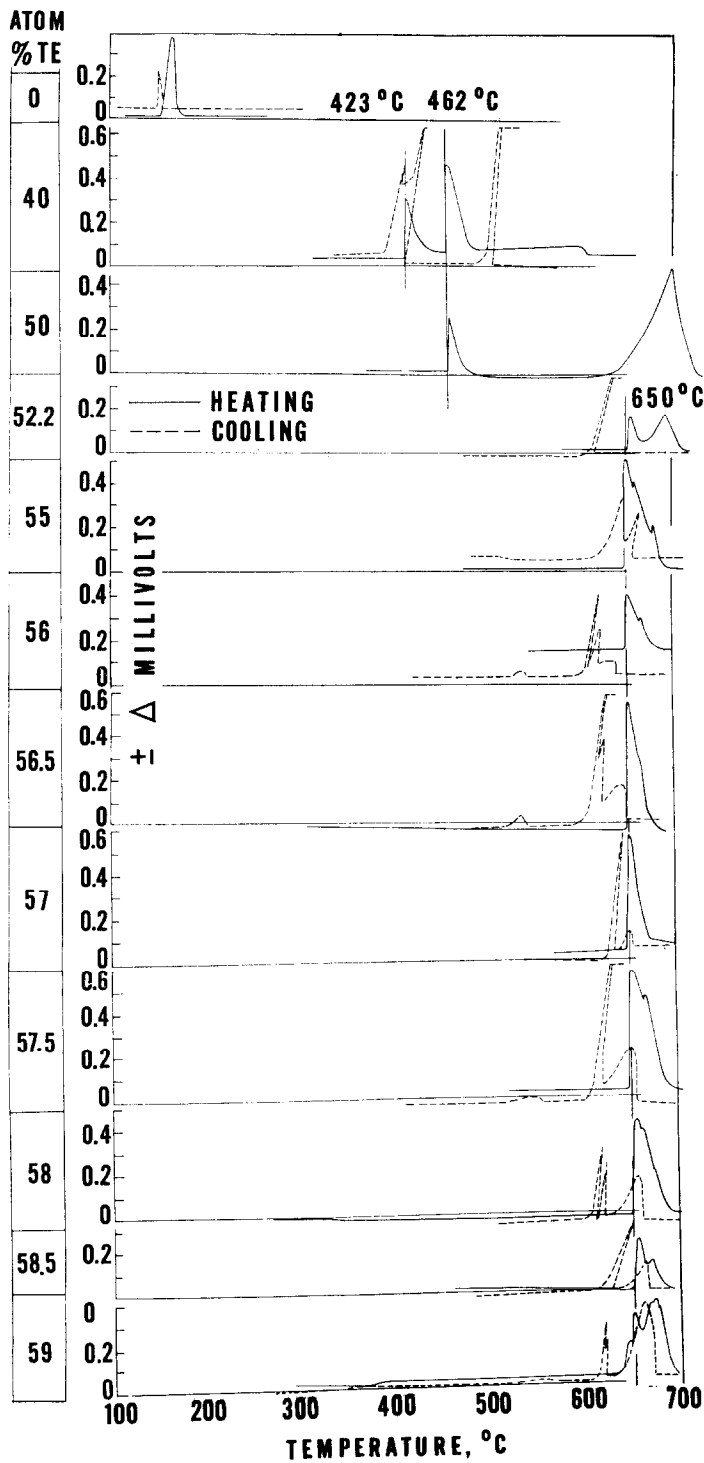
2. EXPERIMENTAL PROCEDURES

All the samples were prepared by pyrosynthesis from pure elements,⁽⁴⁾ and the differential thermal analyses (DTA) were carried out on powdered samples sealed under vacuum in clear quartz tubes with an axial thermocouple well. The methods used have been previously described in more

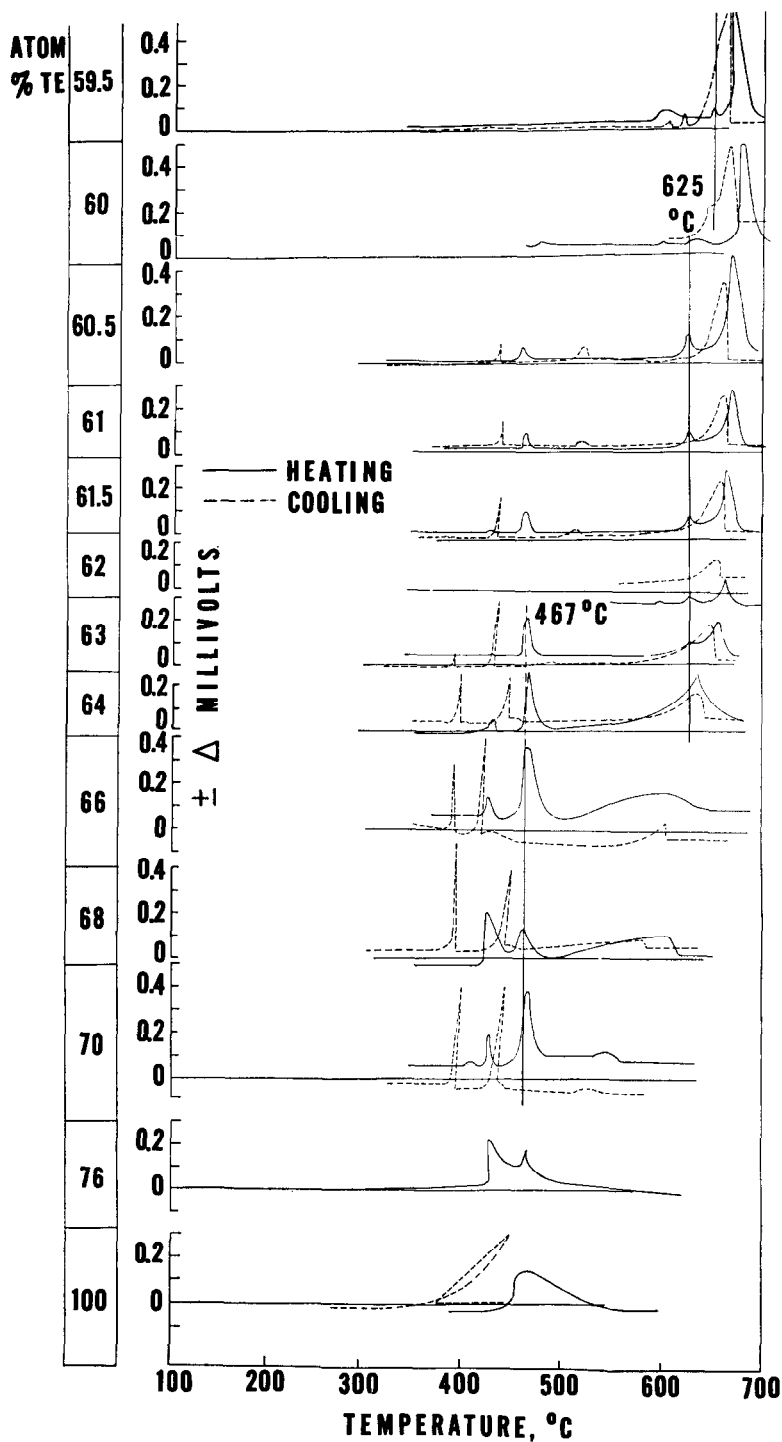
* Contribution No. 7 from The Semiconductor Materials Research Laboratory, The College of Engineering, The University of Michigan, Ann Arbor, Michigan.

† Present address: International Business Machines Corporation, Semiconductor Division, Poughkeepsie, New York.

‡ Present address: Chevrolet Engineering Center, Warren, Mich.



(a)



(b)

FIG. 1. Differential thermal analysis curves for the indium-tellurium system. (a) 0-59 at.% Te; (b) 59.5-100 at.% Te. The solid lines are the heating cycle and the broken lines are the cooling cycle.

detail.^(5,6) Most of the samples were measured using a Leeds and Northrup Model G Speedo-max x - y Recorder to plot differential e.m.f. vs. sample temperature directly. Liquid indium was used as a reference and the samples were heated and cooled at a rate of about $2.5^{\circ}\text{C}/\text{min}$.

Conventional, unidirectional zone refining was used to prepare pure samples of the congruently melting compounds, InTe and In_2Te_3 , starting with compositions on either side of the congruently melting compositions. The solid portions of the ingot were held above 350°C during zone refining to prevent condensation of the Te vapor arising from the molten zone. Large 70 g peritectic samples about 10 in. long were zone leveled by the technique devised by MASON and COOK⁽⁷⁾ to provide sufficient material for further analyses. Zone lengths were maintained at $1\frac{1}{4}$ in. in length and the number of passes was normally from 8 to 10 for each ingot.

When single phase regions of peritectic compounds were obtained, as determined by microscopic examination, they were analysed chemically. The analytical results then were used to determine the composition of the next sample for the zone refiner. When no single phase region was observed, a comparison between two such ingots indicated a variation of the amount of second phase as a function of composition. The composition of the ingots for zone-refining then was adjusted to eliminate the second phase.

The exact composition for each compound of the phase diagram was determined by chemical analysis of zone-refined ingots. A simple analytical technique was developed in which the samples were dissolved in aqua regia, the excess nitric acid was boiled off, and the tellurium ions were reduced by sulfur dioxide. The elemental tellurium precipitate was dried in a moderate vacuum at 60°C to minimize oxidation. The method was reproducible to within 0.1 per cent, using 2 g analytical samples.

Several X-ray powder pattern photographs were taken using a 114.6 mm camera and Cu-K_{α} radiation through a nickel filter to eliminate the Cu-K_{β} radiation. The X-ray film was covered with aluminum foil to reduce spurious radiation effects. Either silicon or germanium was added to each sample to give reference lines on each film.

Electrical conductivity and Hall effect measure-

ments were made on zone-refined, polycrystalline rectangular bars of In_2Te_3 and In_3Te_5 . Measurements were made from room temperature to the melting points in nitrogen or hydrogen. Electrical contacts were made by fusing hot platinum wires onto the samples. The measurements were carried out using conventional d.c. techniques described by LINDERG,⁽⁸⁾ using a 2100 G permanent magnet having a $2\frac{1}{2}$ in. pole face and a $2\frac{3}{4}$ in. gap. The sample holder was made from fired lava (lavite) and has been described in more detail by O'KANE.⁽⁹⁾

3. EXPERIMENTAL RESULTS

The results from most of the 36 DTA runs are plotted in Fig. 1, showing differential thermocouple e.m.f. for chromel-alumel thermocouples as a function of sample temperature and sample composition. The significant, reproducible eutectic temperature at 650°C is indicated, along with the peritectic temperatures at 462, 467 and 625°C . The monotectic at 423°C is also shown. More than 35 zone refining samples were prepared and analysed in these tests.

The results of this work are summarized in the phase diagram shown in Fig. 2, which is a drastic revision of the phase diagram published by HANSEN.⁽²⁾ In going across the diagram the pertinent features are as follows:

(1) As Te is added to the pure In (α -phase) a peritectic at 160°C is formed instead of a eutectic.

(2) The monotectic in the high indium end of the diagram is confirmed by the transition at 423°C .

(3) We find no evidence for the existence of In_2Te . Instead, we believe that the peritectic occurs at about 462°C and 43 at. % Te,* and is In_9Te_7 . This has been substantiated by DTA results and peritectic zone refining experiments.

(4) This work confirms the existence of the congruent compound InTe with a melting point of 696°C , as shown, although its composition actually is at 50.8 at. % Te,* and therefore can be reported more precisely as $\text{In}_{30}\text{Te}_{31}$.

(5) The first new compound in this system is In_3Te_4 which decomposes peritectically at about

* All compositions are reported as atom % Te, based on mol. wt Te = 127.61, mol. wt Indium = 114.82; IUPAC, 1957.

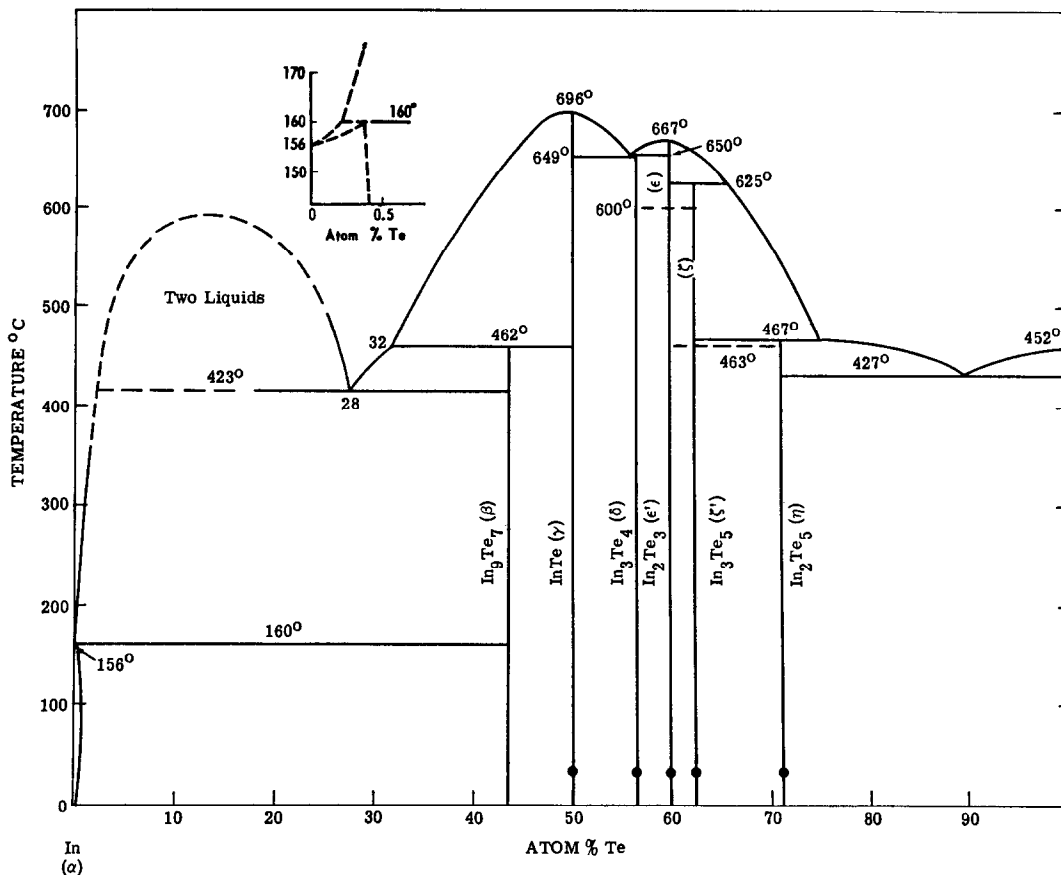


FIG. 2. Phase diagram for the indium-tellurium system.

650°C. This is so close to the 649°C eutectic between InTe and In_3Te_3 that it was overlooked at first. However, on the DTA cooling curves shown in Fig. 1 two supercooled transitions are observed between 56 and 59% Te, which are characteristic of a peritectic-eutectic system. Samples from ingots which were zone refined in the normal manner starting at 58% Te showed an almost homogeneous phase in the center region with composition of about 57.5% Te. From chemical analysis, it was found that the high melting end had a composition of 59.7% Te, and the eutectic had a composition of 56.2% Te. Analysis of X-ray powder patterns on a sample at 56% Te showed some lines characteristic of InTe , but there were in addition a large number of lines which were not characteristic of In_2Te_3 patterns taken on either "ordered" samples or "disordered" samples.

Additional X-ray measurements made on a sample at 57.5% Te showed 59 lines, 12 of which are common to InTe , and 3 of which are common to In_2Te_3 . However, 44 of the lines belong to neither phase, thus confirming the existence of this new compound. HOLMES *et al.*⁽¹⁰⁾ seem to have missed this compound in their investigations.

(6) The compound In_2Te_3 also exists and melts at 667°C, although its composition is actually at 59.7 at.% Te, and therefore can be reported more precisely at $\text{In}_{27}\text{Te}_{40}$. The transformation of In_2Te_3 from a disordered structure to an ordered structure has been reported by many workers, including WOOLLEY *et al.*,⁽¹¹⁾ ZASLAVSIII and SERGEYEVA,⁽¹²⁾ and GASSON *et al.*⁽¹³⁾ ZHUZE *et al.*⁽¹⁴⁾ report an order-disorder transformation in In_2Te_3 at 550°C. From our work the transformation appears to occur between 550 and 600°C.

(7) The presence of the second new compound, In_3Te_5 was indicated by DTA measurements. Samples were prepared by zone leveling techniques, and characterized by chemical, electrical and X-ray analyses. Our X-ray analysis suggests that it has most of the same diffraction lines that have been reported by WOOLLEY *et al.*⁽¹¹⁾ and by ZASLAVSKI and SERGEYEVA⁽¹²⁾ for "ordered" In_2Te_3 . There is a solid-solid transformation in this material which occurs somewhere between 440 and 465°C. Until confirmed by electrical measurements, the DTA results of this transformation were at first interpreted as an extension of the In_2Te_3 peritectic transformation in non-homogeneous DTA samples. It is now apparent that the DTA transitions between 60 and 63% Te have an average temperature of 463°C, whereas those observed between 64 and 70% Te have an average temperature of 467°C.

(8) The compound In_2Te_5 also seems to be confirmed, although its peritectic transformation temperature is at 467°C.

4. ELECTRICAL PROPERTIES AND STRUCTURE OF In_3Te_5

Some electrical conductivity and Hall effect measurements have been made on In_3Te_5 . Measurements were made in nitrogen or hydrogen. ZHUZE *et al.*⁽¹⁴⁾ report that erroneous results are noted when measurements were made in any atmosphere which might contain traces of oxygen. This was attributed to surface oxidation. Hence, hydrogen has been used in all our recent measurements but there has been no detectable change from our earlier measurements. Below about 460°C the measurements are not always reproducible, as shown in Fig. 3. At 460°C there is an abrupt increase in the conductivity by a factor of about 30. The data extend up to about 500°C and suggest an apparent energy gap of about 1.06 eV.

Since the first sample of In_3Te_5 appeared to be non-homogeneous, a section of the ingot was annealed for 7 days in vacuum at 425°C before being measured. Below the transition temperature the results were quite different from those measured on the first sample, and the transition temperature has been decreased by 15°C to 445°C. Above this transition, the measurements are poor but suggest a gap of 0.99 eV, which is acceptably close to the value 1.06 eV measured on

the unannealed sample. Inspection of the samples after measurement showed no evidence that the sample had partially melted or otherwise entered a liquid-containing region of the phase diagram.

The transition in the electrical properties of In_2Te_3 at about 470°C observed by WOOLLEY and PAMPLIN⁽¹⁵⁾ probably arises from contamination of this sample by In_3Te_5 . This seems particularly true since this effect has not been observed by ZHUZE *et al.*,⁽¹⁴⁾ by APPEL,⁽¹⁶⁾ or by us.

An X-ray structure determination on the high temperature form of In_3Te_5 indicates that it has a hexagonal structure, with $c = 3.56 \text{ \AA}$, $a = 13.27 \text{ \AA}$, and $c/a = 0.27$. If all the Te^{-2} atoms in a close-packed array, then there should be 16 Te^{-2} atoms per unit cell, or 3.20 molecules of In_3Te_5 with a theoretical density $\rho = 5.68 \text{ g/cm}^3$. A pycnometer density measurement on this material gave a density, $\rho = 5.87 \text{ g/cm}^3$, which clearly indicates that some of the Te atoms are on cation sites. The semiconducting properties of In_3Te_5 can be explained on the basis of the MOOSER-PEARSON rules⁽¹⁷⁾ by assuming that the formula is actually $\text{In}_{18}^{+3}\text{Te}_{29}^{-2}$. Hence, in each unit cell there are actually 16.55 Te atoms or 3.31 molecules of In_3Te_5 . This compound is in conformity with the Mooser-Pearson formula

$$\frac{n_e}{n_A} + b_A - b_c = 8,$$

where

$$n_e = 3 \times 3 + 5 \times 6 = 39 = \text{number of electrons in valence orbitals/formula wt.}$$

$$n_A = 5 = \text{number of group IVb to VIIb (anion) atoms/formula wt.}$$

$$b_A = 6/30 = 0.2 = \text{average number of anion-anion bonds/anion.}$$

$$b_c = 0 = \text{average number of cation-cation bonds/cation.}$$

The equality is valid since one Te atom in 30 goes into a cation site and makes six bonds to neighboring Te atoms in anion sites.

5. ELECTRICAL MEASUREMENTS ON In_2Te_3

Electrical measurements have been made on a sample of $\text{In}_{27}\text{Te}_{40}$ (In_2Te_3) which was prepared by zone refining of a sample composition $\text{In}_{40.8}\text{Te}_{59.2}$. This sample then is indium-rich, whereas all previously reported measurements on

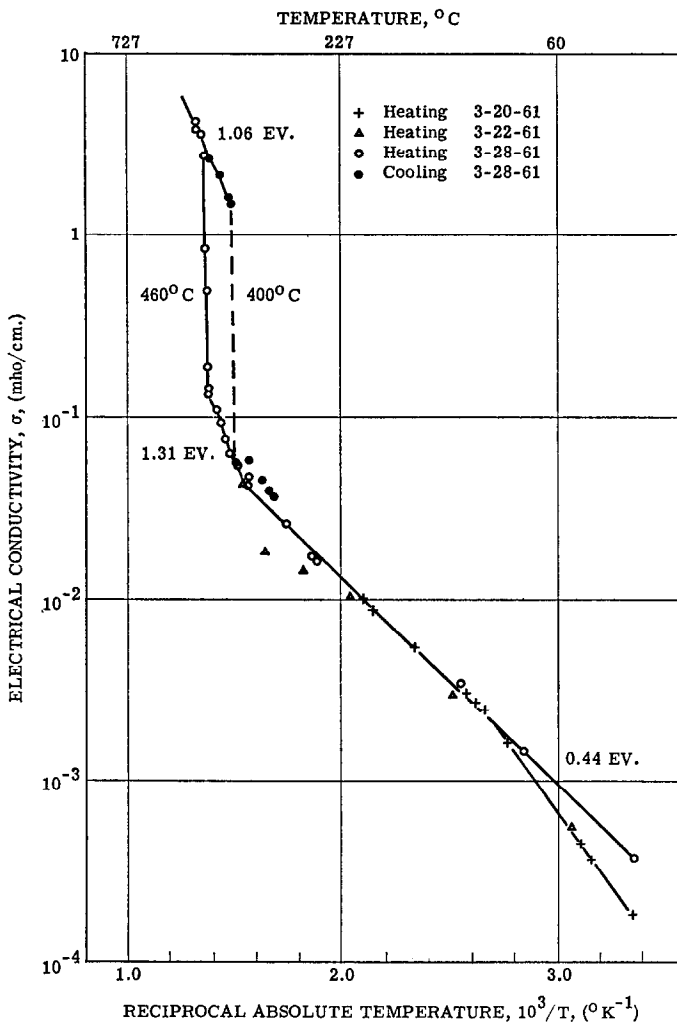


FIG. 3. Electrical conductivity of In_3Te_5 vs. reciprocal absolute temperature.

In_2Te_3 were apparently made on tellurium-rich samples.⁽¹⁴⁻¹⁶⁾

On the first measurement this sample had an apparent energy gap of 2.2 eV from 200 to 500°C. At 500°C, the sample underwent a transition and above about 550°C the energy gap appeared to be 3.6 eV. On cooling, the gap appeared to be equal to 1.1 eV. On reheating the 2.2 eV gap did not appear but the sample retraced the 1.1 eV curve. However, the transformation started at a lower temperature but eventually reproduced the 3.6 eV

curve after considerable instability over a 200°C temperature range (from 300 to 500°C).

The electrical measurements on this compound are sufficiently variable and non-reproducible as to cast severe doubt on their validity, and more measurements are required before the characterization of In_2Te_3 is complete.

Acknowledgements—The authors would like to acknowledge assistance received from Prof. L. THOMASSEN, J. S. COOK, A. N. CURRIM, D. R. JOHNSON, B. M.

KULWICKI, D. F. O'KANE, and G. D. ROSE. This work was supported in part by Project MICHIGAN, under Department of the Army Contract (DA-36-039-SC-78801) administered by the U.S. Army Corps, and in part by the Institute of Science and Technology at the University of Michigan.

REFERENCES

1. KLEMM W. and VOGEL H. U. v., *Z. anorg. Chem.* **219**, 45-64 (1934).
2. HANSEN M., *Constitution of Binary Alloys*, pp. 863-4, 2nd Ed., McGraw-Hill, New York (1958).
3. ZHUZE V. P., ZASLAVSKII A. E., PETRASEVIC V. M., SERGEYEVA V. M., SMIRNOV I. E. and SELYCH A. I., *Proceedings of the International Conference on Semiconductor Physics*, pp. 871-881, Czechoslovak Academy of Sciences, Prague (1961).
4. HOZAK N. L., COOK J. S. and MASON D. R., *J. Electrochem. Soc.* **108**, 105-6 (1961).
6. BARNES C. E. and MASON D. R., *Electrochem. Soc. Electron. Div. Abstr.* **9**, 8-11 (1960).
6. LABOTZ R. J., MASON D. R. and O'KANE D. F., *J. Electrochem. Soc.* **110**, 127 (1963).
7. MASON D. R. and COOK J. S., *J. Appl. Phys.* **32**, 475-477 (1961).
8. LINDBERG O., *Proc. Inst. Radio Engrs* **40**, 1414-1419 (1952).
9. O'KANE D. F., *An Investigation of Ternary Semiconducting Compounds*, Ph.D. Thesis, The University of Michigan, Ann Arbor (1962).
10. HOLMES P. J., JENNINGS I. C. and PARROTT J. E., *J. Phys. Chem. Solids* **23**, 1-5 (1962).
11. WOOLLEY J. C., PAMPLIN B. R. and HOLMES P. J., *J. Less-Common Metals* **1**, 362-376 (1959).
12. ZASLAVSKII A. I. and SERGEYEVA V. M., *Solid-State Phys. (Russian)* **2**, 2872-2880 (1960).
13. GASSON D. B., HOLMES P. J., JENNINGS I. C., PARROTT J. E. and PENN A. W., *Proceedings of the International Conference on Semiconductor Physics*, pp. 1032-1038, Czechoslovak Academy of Sciences, Prague (1961).
14. ZHUZE V. P., SERGEYEVA V. M. and SHELYKH A. E., *Solid-State Phys. (Russian)* **2**, 2858-2871 (1960).
15. WOOLLEY J. C., PAMPLIN B. R., *J. Electrochem. Soc.* **108**, 874-879 (1961).
16. VON APPEL J., *Z. Naturf.* **9a**, 265-267 (1953).
17. MOOSER E. and PEARSON W. B., in *Progress in Semiconductors*, Vol. **5**, pp. 105-139 (edited by GIBSON A. F.). Heyward, London (1960).