UNCLASSIFIED

KAPL-2091

Special

THE EFFECTS OF REACTOR IRRADIATION
ON THE THERMOELECTRIC PROPERTIES
OF LEAD AND BISMUTH TELLURIDES

J. C. Corelli, R. T. Frost

April 1, 1960

R T Frost
Authorized Classifier

June 6th, 1960
Date

General Electric Company
KNOLLS ATOMIC POWER LABORATORY
Schenectady, New York
Operated for the
United States Atomic Energy Commission
Contract No. W-31-109 Eng-52

This document is
PUBLICLY RELEASABLE

UNCLASSIFIED

Larry E. Williams
Authorizing Official
Date: *12/06/2005*

357 02

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government-sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

UNCLASSIFIED

KAPL-2091
Special

<u>Distribution</u>	<u>No. of Copies</u>
AEC, SNROO	50
Caldwell, BH	1
Cashin, WM	1
Corelli, JC	25
Document Library	4
Ehrlich, R	1
Frost, RT	25
Kesselring, KA	1
Penza, NL	1
Plumley, HJ	1
Rumbaugh, EC	1
Selby, JD	1
Warner, MJ	2
Willey, HA	<u>1</u>
Total	115

**DO NOT
PHOTOSTAT**

UNCLASSIFIED

ACKNOWLEDGMENT

The authors wish to acknowledge with gratitude the assistance of those many KAPL contributors whose work made possible the results reported herein. The encapsulation method was largely suggested by Dr. M. Balicki. The experimental measurements of the electrical properties were performed largely by D. M. Amorosi aided by D. J. Ruggiero. Capsule design engineering and most of the details of the irradiation were arranged by the KAPL Irradiation Test Operation. The capsule was fabricated by the Advanced Manufacturing Engineering group. All experimental apparatus was built by the Mechanical Equipment Development Shop.

CONTENTS

	<u>Page</u>
ACKNOWLEDGMENT	v
ABSTRACT	xiii
INTRODUCTION	1
EXPERIMENTAL METHOD AND PROCEDURE	1
Sample Preparation and Encapsulation	2
Measurement of the Electrical Resistivity at Room Temperature	3
Measurement of the Seebeck Coefficient at Room Temperature .	5
Measurement of the Thermal Conductivity at Room Temperature .	7
Measurements of the Seebeck Coefficient and Electrical Resistivity at Elevated Temperatures	8
Description of the Irradiation Procedure	11
Neutron Reactions with Bismuth and Lead Tellurides	11
Measurements of the Gamma-Ray Spectra	14
RESULTS AND DISCUSSION	17
Preliminary Room Temperature Measurements	17
High-Temperature Measurements	20
Presentation of Results in the Form of Seebeck Coefficients vs Temperature	36

ILLUSTRATIONS

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	p-Type Bismuth Telluride Samples before Irradiation (KS-26625)	2
2	Uninstrumented Capsule Assembly (KS-27273)	3
3	Device for Measuring the Electrical Resistivity at Room Temperature (KS-26621)	4
4	Device for Measuring the Seebeck Coefficient at Room Temperature (KS-26624)	6
5	Apparatus for Measuring the Thermal Conductivity (KS-27427) .	8
6a	Apparatus for Measuring the Electrical Resistivity at High Temperatures (KS-28799)	9
6b	Apparatus for Measuring the Seebeck emf at High Temperatures (KS-28799)	9
7	Temperature Regulation Obtained in the High-Temperature Resistivity Apparatus (KS-28800)	10
8	Gamma-Ray Spectra Taken on the Cadmium-Shielded and Unshielded p-Type Lead Telluride Samples 42 Days after the End of Irradiation (KS-28798)	15
9	Gamma-Ray Spectra Taken on the Cadmium-Shielded and Unshielded p-type Lead Telluride Samples 136 Days after the End of Irradiation (KS-29155)	16
10	Resistivity vs Temperature Measurements for Irradiated (Cadmium-Shielded) and Unirradiated n-Type Lead Telluride (KS-28801).	21
11	Seebeck emf vs Temperature Measurements for Irradiated (Cadmium-Shielded) and Unirradiated n-Type Lead Telluride after Annealing (KS-28802)	22
12	Resistivity vs Temperature Measurements for Irradiated (Unshielded) and Unirradiated n-Type Lead Telluride (KS-28803)	23
13	A Measurement of the Rate of Annealing of Resistivity with Time for the Unshielded n-Type Lead Telluride (KS-28804) ,	24

<u>No.</u>	<u>Title</u>	<u>Page</u>
14	Seebeck emf vs Temperature Measurements for Irradiated (Unshielded) and Unirradiated n-Type Lead Telluride after Annealing (KS-28805)	25
15	Resistivity vs Temperature Measurements for Irradiated (Unshielded) and Unirradiated n-Type Bismuth Telluride (KS-28806)	26
16	Seebeck emf vs Temperature Measurements for Irradiated (Unshielded) and Unirradiated n-Type Bismuth Telluride after Annealing (KS-28807)	27
17	Resistivity vs Temperature Measurements for Irradiated (Cadmium-Shielded) and Unirradiated n-Type Bismuth Telluride (KS-28808)	28
18	Seebeck emf vs Temperature Measurements for Irradiated (Cadmium-Shielded) and Unirradiated n-Type Bismuth Telluride after Annealing (KS-28809)	29
19	Resistivity vs Temperature Measurements for Irradiated (both with and without Cadmium Shields) p-Type Bismuth Telluride (KS-28810)	30
20	Seebeck emf vs Temperature Measurements for Irradiated (Cadmium Shielded) and Unirradiated p-Type Bismuth Telluride after Annealing (KS-28811)	31
21	Seebeck emf vs Temperature Measurements for Irradiated (Unshielded) and Unirradiated p-Type Bismuth Telluride after Annealing (KS-28812)	32
22	Seebeck emf vs Temperature Measurements before and after Heat Treatment of Irradiated (Cadmium-Shielded) p-Type Lead Telluride (KS-28813)	33
23	Seebeck emf vs Temperature Measurements for Irradiated (Unshielded) and Unirradiated p-Type Lead Telluride (KS-28814)	34
24	Seebeck Coefficients vs Temperature for the Irradiated (Unshielded) and Unirradiated p- and n-Type Bismuth Tellurides (KS-28815)	35
25	Seebeck Coefficients vs Temperature for the Irradiated (Cadmium-Shielded) and Unirradiated p- and n-Type Bismuth Tellurides (KS-28816)	35

<u>No.</u>	<u>Title</u>	<u>Page</u>
26	Seebeck Coefficients vs Temperature for the Irradiated (Cadmium-Shielded) and Unirradiated p- and n-Type Lead Tellurides (KS-28818)	36
27	Seebeck Coefficients vs Temperature for the Irradiated (Unshielded) and Unirradiated p- and n-Type Lead Tellurides (KS-28817)	36

ABSTRACT

Commercially available specimens of polycrystalline n- and p-type lead telluride* and n- and p-type bismuth telluride** were irradiated in the Engineering Test Reactor at the National Reactor Test Station at Idaho Falls, Idaho. The preirradiation thermoelectric properties are compared with the postirradiation properties. Duplicate samples irradiated with cadmium shields allowed a search to be made for the effects of transmutations.

Total integrated flux-times of 1.5×10^{20} neutrons/cm² (thermal) and 1.6×10^{19} neutrons/cm² (fast, i.e., for neutrons having energies greater than 1 Mev) were accumulated by the specimens during irradiation. The specimen temperature during irradiation was $60 \pm 20^\circ\text{C}$.

The effects of the irradiation on the thermoelectrical properties of these materials were found to be due almost entirely to fast neutrons insofar as most of the damage is healed during heat treatment. One of the expected nuclear reactions caused by thermal neutrons was verified experimentally by performing gamma-ray spectroscopy on each irradiated sample. Increases in the electrical resistivity for irradiated n-type PbTe and Bi₂Te₃ were found to anneal at temperatures below 200°C . For irradiated n-type PbTe most of the increase in the electrical resistivity and Seebeck coefficient can be explained by the decrease in carrier concentration, which was determined by Hall coefficient measurements. Measurements of the electrical resistivity and Seebeck coefficient as a function of temperature for irradiated and unirradiated samples cut from the same ingot are given for all materials except p-type PbTe. For the latter sample only the measurements of the Seebeck coefficient are given.

*From the Minnesota Mining & Manufacturing Company, St. Paul, Minnesota.

**From the Merck Company, Rahway, New Jersey.

THE EFFECTS OF REACTOR IRRADIATION ON THE THERMOELECTRIC PROPERTIES OF LEAD AND BISMUTH TELLURIDES

INTRODUCTION

The recent progress made in the development of semiconductors for use as thermoelectric materials has prompted many experiments and research in this relatively new area. Two materials which have received the most attention for application in thermoelectric cooling and thermoelectric power generation for temperatures below about 500°C are lead telluride and bismuth telluride. Both of these materials are available in relatively large quantities and each can be manufactured with reasonably similar thermoelectric properties from one batch to another.*

An obvious area of interest is the effect of nuclear radiations on the physical properties of these semiconductors. Irradiation damage experiments carried out previously on silicon and germanium have shown that relatively large changes occur in the properties of these lightly doped semiconductors after relatively modest reactor flux exposures. The heavy doping which is characteristic of most of the thermoelectric materials recently developed for power generation suggests that these materials may tend to be, as a class, more resistant to the effects of irradiation. In the experiments described herein lead and bismuth tellurides of both n and p types were exposed at 60°C to a reactor neutron flux dose of approximately $1.4 \times 10^{20} \text{ cm}^{-2}$ thermal and $1.6 \times 10^{19} \text{ cm}^{-2}$ fast (above 1 Mev). The radiation-induced changes in the thermoelectric properties proved to be essentially annealable at temperatures in the range of 150 to 200°C for most of the samples studied.

EXPERIMENTAL METHOD AND PROCEDURE

It is convention to describe the efficacy of a thermoelectric material by specifying its so-called figure of merit, Z , defined by

$$Z = \frac{S^2}{\rho K},$$

*PbTe is available from Minnesota Mining & Manufacturing Company, St. Paul, Minnesota. Bi₂Te₃ is available from Merck Company, Rahway, New Jersey.

where S is the Seebeck coefficient in $\mu\text{volts}/^\circ\text{C}$, ρ is the electrical resistivity in ohms-cm, and K is the thermal conductivity in $\text{watts}/\text{cm}^\circ\text{C}$. These three parameters specify completely the maximum efficiency of a material for producing power when used over a given temperature range; however, they do not give the whole story. One must bear in mind the fact that K is related to ρ because the total thermal conductivity consists of two parts: namely, the electronic component and the lattice component. The former component is related to the electrical conductivity via the Wiedemann-Franz law.[†]

For this experiment the changes in the properties mentioned above were measured subsequent to a reactor irradiation. From such an experiment some insight can be gained regarding the mechanism of radiation damage, its magnitude, and whether or not the damage is annealable at reasonably low temperatures (e.g., less than 400 to 500°C).

Sample Preparation and Encapsulation

For the first series of high-flux reactor irradiation experiments on thermoelectric materials polycrystalline samples of n- and p-type PbTe and n- and p-type Bi_2Te_3 were used. Specimens 1/2 in. long were cut from 1/4-in.-diameter cylinders, and scraps resulting from the cutting were used for chemical analysis of the constituents.

FIGURE 1. P-TYPE BISMUTH TELLURIDE SAMPLES
BEFORE IRRADIATION

In order to ensure that no oxide layer or film of any kind was present on the sample surface prior to electrical measurements, all samples were cleaned by use of a dental grit-blasting apparatus.* Subsequent to this cleaning the samples were handled with tweezers and the preirradiation room temperature electrical measurements (S and ρ) were made. Typical samples of p-type Bi_2Te_3 after the final preparation are shown in Figure 1. For each sample irradiated a calibration sample cut from the

same ingot of PbTe or Bi_2Te_3 was used to cross-check with postirradiation measurements. Such samples were designated as control samples and were not irradiated.

Eight specimens of PbTe and Bi_2Te_3 were irradiated in this first experiment. Duplicate samples irradiated with and without cadmium shields allowed a search for effects of transmutation. The irradiations were

[†]The constant of proportionality is the same as that for metals only in the degenerate case.

*S. S. White Dental Grit Blaster.

FIGURE 2. UNINSTRUMENTED CAPSULE ASSEMBLY

TOP: EXPLODED VIEW
 CENTER: WELDED SAMPLE
 BOTTOM: CADMIUM-COATED SAMPLE

performed in the Engineering Test Reactor (ETR) at the National Reactor Test Station at Idaho Falls; the samples were inserted into the reactor on September 28, 1959 and removed on November 30, 1959.

In order to keep the specimen temperature as low as possible during irradiation (gamma-ray heating is approximately 2 to 4 watts/gm), a special encapsulation technique* was developed. Essentially this technique consisted of tightly wrapping aluminum jackets around the specimens to form a capsule and to ensure good thermal contact. The capsule was filled with helium gas and sealed. Appropriate flux monitors in the form of cobalt-aluminum and nickel wires were inserted inside the capsule. The cadmium shielding was sprayed onto the outside of the aluminum jacket of four samples to approximately 40 mils thick. The cadmium was subsequently plated with nickel. This method ensured the best cooling of the samples with reactor coolant. This uninstrumented capsule assembly is shown in Figure 2.

Measurement of the Electrical Resistivity at Room Temperature

The electrical resistivity of all samples was measured by use of a standard, dc, four-probe technique. The application of this technique to the samples described above involves the measurement of a voltage drop between two points on the cylindrical surface when a known current is

*By D. W. Linde, H. K. Ruhl, G. W. Smith, and H. L. Zoch of the Irradiations Group at KAPL.

flowing in the direction of the axis of the cylinder. The current flowing in the sample was obtained by measuring the voltage developed across a known standard resistor. Both voltages were measured with precision Rubicon potentiometers.

A photograph of the device used for making the electrical resistivity measurements at room temperature is shown in Figure 3 below. The two voltage-measuring probes are connected to a micrometer, which is spring-loaded and hinged so that it can swing down and allow the probes to make good electrical contact with the specimen. To ensure positive contact, one of the voltage probes is spring-loaded so that it accommodates itself vertically when the micrometer is lowered to the measuring position. The travel screw of the micrometer was calibrated with an optical comparator and was found to agree with the vernier indicator to within 1%.

The current is supplied to the sample by means of the two horizontal probes shown in Figure 3. One of the probes is spring-loaded with a calibrated spring to provide the same contact pressure for all measurements. To ensure good electrical contact between the current-carrying electrodes and the specimen, the electrodes were fabricated from a large number of nickel (in a later model silver was used) wires which were made to form a stiff brush $3/16$ in. long and $1/4$ in. in diameter. The brush accommodates

FIGURE 3. DEVICE FOR MEASURING THE ELECTRICAL RESISTIVITY AT ROOM TEMPERATURE

KAPL-2091

itself to deviations from flat and square specimen surfaces and in this way provides good electrical contact. That these electrodes provided parallel current lines through the samples was shown by repetitive resistivity measurements in which typical samples were successively rotated about their cylindric axes between the measurements.

Since the thermoelectric materials studied here have relatively large Seebeck coefficients (~ 100 to $200 \mu\text{volts}/^\circ\text{C}$), very small differences in temperature between the voltage contact probes can introduce a spurious voltage in the resistivity measurement. Such temperature differences arise, for example, from Peltier heating or merely from handling the electrodes. The latter effect was eliminated by using Bakelite tongs to separate the electrodes when the samples are changed, while the former effect was reduced by using small currents and reversing the current. Thus, two voltage measurements are obtained (the average is used) for current flowing first in one direction and then reversed.

In order to minimize temperature effects, all standard cells, potentiometer batteries, standard resistors, and current-reversing switches were mounted inside a large, thermally insulated box. All electrical leads were kept as close together as possible, which tends to balance out thermal voltages induced in the lead wires, and a lucite box was placed over the resistivity device to minimize convection currents at the sample during measurement.

TABLE 1. AVERAGE ELECTRICAL RESISTIVITY MEASUREMENTS AT ROOM TEMPERATURE FOR UNIRRADIATED SAMPLES

Sample	Electrical Resistivity, ohm-cm
n-type PbTe	4.5×10^{-4}
p-type PbTe	3.6×10^{-4}
n-type Bi_2Te_3	5.1×10^{-4}
p-type Bi_2Te_3	18×10^{-4}

The rms error in the measurements on a particular sample was obtained by placing it in different orientations in the sample holder (Figure 3) and remeasuring. This resulted in the following rms errors: PbTe - 3%, Bi_2Te_3 - $\lesssim 8\%$. Some average electrical resistivity measurements at room temperature for these specimens prior to irradiation are given in Table 1.

Measurement of the Seebeck Coefficient at Room Temperature

The Seebeck coefficients of these specimens were obtained by measuring the voltage generated when a temperature difference existed between two points of the material. The temperature difference which gives rise to the Seebeck emf was accomplished by bringing a small heater in contact with a limited area of the sample surface. The temperatures were measured by means of thermocouples, one leg of each serving simultaneously as a voltage-measuring probe. The Seebeck coefficient was then obtained by taking the ratio of the voltage difference to the temperature difference.

FIGURE 4. DEVICE FOR MEASURING THE SEEBECK COEFFICIENT AT ROOM TEMPERATURE

Figure 4 is a photograph of the device used for measuring the Seebeck coefficient at room temperature. The probe at the left side contains a copper-constantan thermocouple which is beaded at the tip. This electrode is spring-loaded to accommodate samples at various lengths and also ensures positive probe contact with the sample. The probe at the right contains a heater winding in addition to a copper-constantan thermocouple. The heater is used to raise the temperature on the left-side contact point (12°C was usually used). The thermocouple voltages indicative of the temperatures were measured by a Leeds and Northrup potentiometer, and the Seebeck emf developed between the

TABLE 2. AVERAGE SEEBECK COEFFICIENT MEASUREMENTS AT ROOM TEMPERATURE FOR UNIRRADIATED SAMPLES

Sample	Seebeck Coefficient, $\mu\text{volt}/^{\circ}\text{C}$
n-type PbTe	$-(130 \pm 2.6)$
p-type PbTe	$+(57.6 \pm 1.2)$
n-type Bi_2Te_3	$-(163 \pm 4.9)$
p-type Bi_2Te_3	$+(192 \pm 4)$

two ends of the sample (open-circuit voltage) was measured with a precision potentiometer. One copper lead from each copper-constantan thermocouple was used for this latter measurement.

For these measurements the rms error obtained by orienting the sample in various positions in the device was less than 3% for the PbTe and less than 5% for the Bi_2Te_3 . Some average room temperature Seebeck coefficients before irradiation are given in Table 2.

Measurement of the Thermal Conductivity at Room Temperature

A device which makes use of the Powell* comparator technique for measuring thermal conductivities has been built. Except for minor modifications it is similar to the one built at the Temperature Measurement Laboratory** of the General Electric General Engineering Laboratory. The basic idea of this technique is to compare the rate of cooling of metal spheres in contact with two different specimens. This is done by heating the spheres, which are made of silver, to some temperature higher than that of the specimens. Thermocouples are located at the center of the spheres, which are kept in close proximity to the specimens to be measured. The heated silver spheres are alternately brought into contact with each specimen, and the rate of cooling is measured by the voltage developed in the differentially connected thermocouples. The magnitude of the thermal conductivity is then measured by the voltage signal (of the order of 10 to 20 μ volts for the thermoelectric materials) developed during cooling. The method is based on the fact that the thermal conductivity is proportional to the rate at which a substance absorbs heat when it is in contact with a higher-temperature heat source.

A photograph of the apparatus is shown in Figure 5. The apparatus is built on a stand equipped with a bell jar for the evacuation of air and purging with an inert gas for measurements at temperatures above ambient. To date only room temperature measurements have been made. The two upper areas support the silver balls, around which are wound the heaters. The samples are placed into the wells shown immediately below the silver balls. The wells are made of stainless steel and are heated by windings of nichrome wire (not visible) located inside the heat shields. The contacts are made by actuating a solenoid, which allows a shaft to fall slowly and the silver ball to touch, alternately, either specimen.

An inherent difficulty arises from this method which is characteristic of all such comparator techniques: namely, the need for standards whose thermal conductivities lie in the required range, from about 10 to 30 milliwatts/cm-°C. Such standards of small dimensions are not available at present. The only standard which we have in use is a small Pyrex sample having a thermal conductivity of 11 milliwatts/cm-°C. This was obtained from the National Bureau of Standards by Mr. A. Dahl, of the General Electric General Engineering Laboratory.

*R. W. Powell, "Experiments Using a Simple Thermal Comparator for Measurement of Thermal Conductivity, Surface Roughness and Thickness of Foils or of Surface Deposits," J. Sci. Instr. 34 (December 1957), 485-492.

**The assistance of H. Robinson, A. Dahl, and M. Flanagan are gratefully acknowledged.

FIGURE 5. APPARATUS FOR MEASURING THE THERMAL CONDUCTIVITY

Measurements of the Seebeck Coefficient and Electrical Resistivity at Elevated Temperatures

Detailed descriptions of the two pieces of apparatus used for measuring resistivity and Seebeck coefficients at elevated temperatures are shown in Figures 6 and 6b, respectively. The Seebeck coefficients were measured as a function of temperature as follows. The cold-junction thermocouple was allowed to come to thermal equilibrium with the copper block kept at about 0°C by the ice-water mixture. The hot-junction temperature was increased by slowly supplying electric current to the soldering iron heater element. At various hot-junction temperatures the open-circuit voltage (Seebeck emf) developed between the hot- and cold-junction thermocouples was measured with a Rubicon precision potentiometer. During the course of a run, which consisted of measuring the Seebeck emf vs Temperature (up to $\sim 400^{\circ}\text{C}$ for Bi_2Te_3 and $\sim 580^{\circ}\text{C}$ for PbTe), the cold-junction temperature was kept at $1.5 \pm 1^{\circ}\text{C}$ by continually monitoring and adding ice to the mixture.

FIGURE 6a. APPARATUS FOR MEASURING THE ELECTRICAL RESISTIVITY OF THERMOELECTRIC MATERIALS AT HIGH TEMPERATURES

FIGURE 6b. APPARATUS FOR MEASURING THE SEEBECK EMF OF THERMOELECTRIC MATERIALS AT HIGH TEMPERATURES

It was found that this relatively simple apparatus (although requiring two people to operate) proved to be extremely useful and reproducible (better than $\sim 3\%$). The data are accumulated in the form of emf vs temperature curves. In order to extract from this the Seebeck coefficient vs temperature, one needs only to differentiate the experimentally determined emf (E) vs temperature (T) curves, since the Seebeck coefficient is obtained from

$$S(T_0) = \left(\frac{\Delta E}{\Delta T} \right)_{T_0}.$$

By the adherence to convention, the emf sign is taken to be positive when the hot junction is negative with respect to the cold junction. This computation was conveniently done by using an IBM-704 code which yields explicitly the derivative from a well-behaved experimental "curve."

The resistivity measurements as a function of temperature were carried out in a vacuum (pressure $\approx 10^{-5}$ mm Hg) to prevent surface oxidation of the sample. The elimination of this difficulty was considered important because of extraneous oxide layers giving rise to large contact resistances. The design of the apparatus utilizes the standard four-probe technique in which all probes are spring-loaded to establish good contact with the sample. The sample temperature was obtained by averaging the temperatures measured by the two thermocouples. The average temperature was almost always within 2% of the reading of either thermocouple, whose temperatures were measured

with a precision-compensated Leeds and Northrup thermocouple potentiometer. The current through the sample and the resistivity voltage signal were measured with a precision Rubicon Six-Dial Thermofree potentiometer. During the course of a run it was important to increase the furnace temperature slowly in order to minimize temperature transients. The apparatus is capable of reaching temperatures of 800 to 1000°C.

As an alternative to a resistivity vs temperature run it was possible with this apparatus also to control the temperature and obtain a measurement of resistivity vs time. This was done on one of the samples to measure the rate of annealing at a fixed temperature. For this experiment one thermocouple serves as a sensing element and is connected to a control circuit which has been preset to some temperature. The control circuit operates a relay which allows current to flow in the furnace windings only if the furnace temperature is lower than the control temperature. The relay shuts off the current flow to the furnace when its temperature is equal to or greater than the control temperature. The other thermocouple in the furnace is connected to a precision potentiometer for an accurate temperature measurement. A typical temperature vs time experiment is shown in Figure 7, which illustrates the degree of control which can be obtained by this method. With this technique it was relatively easy to keep the furnace temperature of 155°C constant to within 1°C during a 6-hr period.

FIGURE 7. TEMPERATURE REGULATION OBTAINED IN THE HIGH-TEMPERATURE RESISTIVITY APPARATUS

Description of the Irradiation Procedure

In Table 3 are listed the sample type, the sample code designation (which gives the ingot number), the condition during irradiation, nominal doping, radiation-induced doping, and the fast and thermal neutron flux times measured by cobalt and nickel flux monitors. For all cases the monitor, in the form of cobalt-aluminum and nickel wires, was located within 1/8 in. of the sample whose total integrated flux-time was to be measured. The fast flux is to be taken to include all neutrons of energies greater than about 1 Mev.

The results of the flux measurements given in Table 3 indicate that the four unshielded specimens received a substantially lower total fast flux than the shielded ones. This can be explained by the fact that the shielded and the unshielded specimens were located 4 in. apart in the irradiation basket. In relation to the above the rather complex history of this particular ETR cycle must be borne in mind also (i.e., inadvertent reactor shutdowns for periods of several days). No thermal flux-time values are quoted for the cadmium-shielded specimen, since the cadmium thickness was sufficient to absorb all neutrons of energies less than about 0.4 ev.

The capsules containing the specimens were so designed that the temperature of the PbTe and Bi₂Te₃ samples was kept at $60 \pm 20^\circ\text{C}$ during irradiation. This was done to prevent the possible annealing of radiation damage at higher temperatures. The details of the first irradiation given in Table 3 are included for purposes of completeness in specifying each specimen in the text which follows.

Neutron Reactions with Bismuth and Lead Tellurides

The principal nuclear reactions anticipated in a reactor environment between neutrons and the nuclear constituents of the thermoelectric materials irradiated in this experiment are discussed below.

Thermal Neutron Capture in Tellurium

The principal nuclear reactions which lead to the formation of new chemical species are listed below:

The thermal cross section for this reaction is 0.8 barn, and the natural isotopic abundance of Te¹²⁶ is 18.7%, so that in an integrated thermal flux of 1.5×10^{20} neutrons/cm², the number of iodine atoms produced per initial atom of tellurium is

$$(0.8 \times 10^{-24})(0.187)(1.5 \times 10^{20}) = 2.2 \times 10^{-5}.$$

In addition, some Te¹²⁷ with a Te¹²⁶ cross section of 0.09 barn

TABLE 3. SPECIFICATION OF SPECIMEN TYPE AND CODE DESIGNATION,
DOPING, FLUX-TIMES, AND CONDITION DURING IRRADIATION

Specimen	Condition during Irradiation	Code Designation	Nominal Doping	Radiation-Induced Doping, mole % I ₂	Total Integrated Flux-Times	
					thermal nvt × 10 ²⁰	fast (>1Mev) nvt × 10 ¹⁹
n-type PbTe	Cadmium shielded	B-7L56 Sample A	0.055 mole % PbI ₂	-	-	1.9
	Unshielded	B-7L56 Sample C	0.055 mole % PbI ₂	0.0017	1.7	1.7
p-type PbTe	Cadmium shielded	B-2L59 Sample A	0.5 at.% Na	-	-	1.9
	Unshielded	B-3L59 Sample B	0.5 at.% Na	0.00097	0.97	1.1
n-type Bi ₂ Te ₃	Cadmium shielded	202C Sample 5	0.5 mole % CuI	-	-	1.6
	Unshielded	202C Sample 2	0.5 mole % CuI	0.0042	1.4	1.4
p-type Bi ₂ Te ₃	Cadmium shielded	204F Sample 5	None	-	-	2.0
	Unshielded	208I Sample 4	None	0.0039	1.4	1.6

is produced as the 110-day isomer, which ultimately decays also to stable I^{127} . Since this amount is an order of magnitude lower than the Te^{127} produced directly as the 9.3-hr isomer, it will be neglected henceforth.

Here the thermal cross section is 0.14 barn, and the natural abundance of Te^{128} is 31.8%, so that the amount of I^{129} produced per initial atom of tellurium is 0.6×10^{-5} . In addition, some Te^{129} with a cross section of 0.016 barn is produced as the 33-day isomer, which ultimately decays also to I^{129} . Since this again is an order of magnitude smaller than the amount produced through the short-lived isomer, it will be neglected. The I^{129} has a half-life of 1.7×10^7 years and so can be regarded as essentially stable.

In the above reaction the thermal absorption cross section is 0.2 barn, and the natural abundance of Te^{130} is 34.4%, so that the number of I^{131} atoms produced per initial tellurium atom is 1.0×10^{-5} . Again there is a branch of the reaction which proceeds through a longer-lived isomer with a cross section an order of magnitude lower than that of the main reaction. The smaller branch is again neglected.

Summing up the above yields, we find that the iodine concentration for times following the irradiation which are at least several times as long as the 8-day lifetime of I^{131} will be approximately 3×10^{-5} atoms for every tellurium atom present initially. This amount corresponds to 0.0015 mole % I_2 in $PbTe$ and 0.0045 mole % I_2 in Bi_2Te_3 .

In addition, there are a number of transmutations of one stable isotope of tellurium to another stable isotope. Since they are not expected to lead to any significant differences in the electrical properties of the material, these reactions can be neglected for the present purposes.

Neutron capture in the Te^{120} isotope, which would be expected to lead to 2×10^{-5} atoms of Sb^{121} if one assumes the upper bound (140 barns) previously published for the thermal capture cross section of Te^{120} , can now be neglected, because of the recent KAPL measurement of this cross section as 2.5 ± 1.0 barns.*

*W. E. Moore, unpublished data, Knolls Atomic Power Laboratory.

Resonance Capture in Tellurium

Recent work by C. J. Heindl at Columbia University* shows that the only measurable contribution to resonances in tellurium up to 250 volts is attributed to isotopes 123 and 125, which transmute to other stable isotopes of tellurium upon neutron capture. Therefore, the contributions of resonance capture to changes in electrical properties during neutron irradiation can be neglected.

Neutron Capture in Lead and Bismuth

Lead and bismuth have resonance integrals of 0.1 and 0.5 barn, respectively. From these data it is estimated that transmutations due to resonance capture in these elements in the ETR spectrum are an order of magnitude smaller in amount than transmutations due to thermal neutron capture in tellurium.

(n,p) and (n,2n) Reactions

An estimate** based on neighboring nuclei indicates that the (n,p) and (n,2n) cross sections for lead and tellurium are probably less than 100 mbarn averaged over a fission spectrum. If this assumption is correct, these reactions can be neglected.

Burnup of Initial Doping Agents

The burnup of the iodine initially present in the 0.05 mole % n-type materials and the sodium initially present in the 0.5 at.% p-type PbTe is calculated as approximately 0.2% of the initial amount. This estimate includes resonance capture in the iodine, which has a resonance integral of 130 barns. The daughter substance formed is stable Xe^{128} , which, as a noble gas, is not expected to have any effect on carrier concentration.

Measurements of the Gamma-Ray Spectra

In order to check the occurrence of the principal neutron reactions with bismuth and lead tellurides which are discussed above, some gamma-ray spectroscopy was performed on each sample. A radioactive "source" of each of the irradiated samples (8) given in Table 3 was prepared by lightly rubbing the specimen with a small piece of emery cloth. The pieces of cloth containing the activity were put into individual polyethylene bottles, which served also as convenient beta-particle shields. No absolute counting was attempted; hence, relative quantities were unimportant. The gamma-ray spectra were measured with a 2- x 2-in. NaI(Tl) scintillation crystal optically coupled with Dow-Corning 200 fluid to a Dumont 6292 photomultiplier tube. The light

*C. J. Heindl, "Neutron Cross Sections of Tellurium," Columbia University (Thesis), June 30, 1959.

**J. R. Stehn, private communication, Knolls Atomic Power Laboratory.

pulses developed in the crystal by the various gamma-ray interactions were fed to an RCL 256-channel pulse height analyzer. In this way rapid measurements of the gamma-ray spectra (intensity vs energy) were made. The scintillation spectrometer was calibrated in terms of gamma-ray energy vs pulse height by using gamma rays of known energies arising from the decay of Co^{60} , Cs^{134} , and Cs^{137} .

Typical gamma-ray spectra which resulted from the cadmium-shielded and unshielded p-type PbTe are shown in Figure 8 below. It is significant to point out here that all other irradiated specimens exhibited exactly these same type of spectra. Consequently, the principle gamma activities induced by the irradiation in all specimens are shown in Figure 8. The gamma rays from nuclear reactions involving Te^{126} and Te^{128} are not "seen" in this spectrum because the short-lived radioactive daughters I^{127} and I^{129} have decayed completely, since these spectra were taken 42 days after the end of the irradiation. However, we do see the reaction

from the 0.070- and 0.360-Mev I^{131} gamma rays present in the spectrum. It is seen that the 0.36-Mev gamma ray is suppressed in intensity relative to the 0.159-Mev gamma ray for the cadmium-shielded sample. This phenomenon is not fully understood at present. This experimental result would imply the existence of resonance levels in the Te^{122} nucleus. This

FIGURE 8. GAMMA-RAY SPECTRA TAKEN ON THE CADMIUM-SHIELDED AND UNSHIELDED p-TYPE LEAD TELLURIDE SAMPLES 42 days AFTER THE END OF IRRADIATION

plausible and probably true statement needs more experimental verification. These measurements will be repeated on the specimens which are being irradiated to a higher flux dose at present.

A spectrographic analysis of the cadmium shield (which was sprayed onto the aluminum capsule) indicated that the cadmium content was 97% by weight. This would prove the relative opacity of the cadmium shields to thermal neutrons (cutoff energy ≈ 0.4 ev). The 0.159-Mev peak due to the Te^{123} isotope is entirely expected, but unimportant, since the final product is a stable isotope of tellurium which does not affect the electrical properties of the material. The new chemical species formed during irradiation which are of prime importance are those leading to the formation of iodine, since it is used as a doping agent in n-type Bi_2Te_3 and PbTe . The gamma-ray spectra of the same samples shown in Figure 8, measured 136 days after the end of the irradiation, are shown in Figure 9 below. It can be seen that only the 0.159-Mev gamma ray from Te^{123} (140 day half-life) is present, while the I^{131} 8-day activity has decayed completely. This result makes the above discussion more definitive.

It can be concluded that telluride compounds irradiated to comparable or higher burnups will not give rise to important gamma rays of energies greater than 0.4 Mev.

FIGURE 9. GAMMA-RAY SPECTRA TAKEN ON THE CADMIUM-SHIELDED AND UNSHIELDED p-TYPE LEAD TELLURIDE SAMPLES 136 days AFTER THE END OF IRRADIATION

RESULTS AND DISCUSSION

Preliminary Room Temperature Measurements

The first postirradiation measurements made were of the Seebeck coefficients, electrical resistivities, and thermal conductivities at room temperature. These measurements are compared with preirradiation values. Because of the high level of induced radioactivity, these first measurements were made with remote-handling equipment in a "hot" cell at the KAPL Radioactive Materials Laboratory.

The results of measurements of the Seebeck coefficient and electrical resistivity at room temperature are presented in Table 4. S_0 and ρ_0 refer to values of the Seebeck coefficient and electrical resistivity measured before irradiation, while S_1 and ρ_1 refer to the values measured after irradiation. All the measurements were made at the ambient hot cell temperature of about 30°C.

TABLE 4. COMPARISON OF PRE- AND POSTIRRADIATION ELECTRICAL PROPERTIES OF PbTe AND Bi₂Te₃ AT ROOM TEMPERATURE BEFORE ANNEALING

Specimen	Condition during Irradiation	S_0 , $\mu\text{volts}/^\circ\text{C}$	S_1 , $\mu\text{volts}/^\circ\text{C}$	S_1/S_0	ρ_1/ρ_0
PbTe	n-type Cadmium-shielded	-127	-243	+1.91	10 $\pm$ 1
	n-type Unshielded	-137	-231	+1.69	10 $\pm$ 1
	p-type Cadmium-shielded	+59.2	+88.3	+1.49	25 $\pm$ 5
	p-type Unshielded	+60.9	+105	+1.74	22 $\pm$ 5
Bi ₂ Te ₃	n-type Cadmium-shielded	-163	-170	+1.04	2.6 $\pm$ 0.3
	n-type Unshielded	-149	-170	+1.16	5 $\pm$ 1
	p-type Cadmium-shielded	+171	-140	-0.82	1.2 $\pm$ 0.2
	p-type Unshielded	+192	-202	-1.05	2.0 $\pm$ 0.2

S_0 = Seebeck coefficient before irradiation

S_1 = Seebeck coefficient after irradiation

ρ_0 = electrical resistivity before irradiation

ρ_1 = electrical resistivity after irradiation

The preliminary relative measurements of the thermal conductivities of all irradiated samples at room temperature exhibited substantial decreases. This is consistent with the fact that the electrical conductivity of each sample was decreased (Table 4) as a result of the irradiation. Since standards are not available, we cannot quote absolute values of the thermal conductivity, which were obtained by using the thermal comparator described previously. The results of the thermal conductivity measurements at room temperature are given in Table 5. K_1 is the thermal conductivity

TABLE 5. COMPARISON OF PRE- AND POSTIRRADIATION MEASUREMENTS
OF THERMAL CONDUCTIVITY BEFORE ANNEALING

Specimen		Condition during Irradiation	Sample Temperature during Measurement, °C	K_1/K_0 †
PbTe	n-type	Cadmium-shielded	35	0.84
	n-type	Unshielded	35	0.80
	p-type	Cadmium-shielded	34.8	0.81
Bi ₂ Te ₃	n-type	Unshielded	36.2	0.88

K_0 = thermal conductivity of the unirradiated sister sample

K_1 = thermal conductivity after irradiation

†Not corrected for instrumental nonlinearities.

after irradiation, while K_0 is the thermal conductivity of the unirradiated "sister" sample taken from the same ingot. It was not possible to measure other samples because they were partially broken, and hence the results would have been much less accurate.

The relative thermal conductivity values are preliminary because the availability of only a single standard of thermal conductivity has so far precluded calibration for expected nonlinearities between conductivity and signals.

The first Hall coefficient measurements* were made on the irradiated and unirradiated samples at room temperature (before annealing). This measurement allows one to determine the carrier concentration and the carrier type. For the thermoelectric samples under consideration here the carrier concentrations are of the order of $10^{19}/\text{cm}^3$. For such highly doped materials with high carrier concentrations, the Hall effect gives rise to relatively small signals. This condition requires that "IR" errors and spurious thermomagnetic or galvanomagnetic effects be minimized. In the measurements given here standard dc techniques were employed, and the experiments were performed with emphasis on the elimination of extraneous signals. The results for room temperature Hall coefficient measurements before annealing are given in Table 6.

By referring to Table 4 one can say that the relatively small quantity of radiation damage (compared with that experienced in semiconductors of much lower carrier concentrations, of the order 10^{16} to $10^{17}/\text{cm}^3$) suffered

*Measurements made by Dr. F. A. White of the Technical Operations group at KAPL.

TABLE 6. HALL COEFFICIENTS OF IRRADIATED AND UNIRRADIATED
LEAD AND BISMUTH TELLURIDES

Specimen		Condition during Irradiation	Hall Coefficient, R , $\text{cm}^3/\text{coulomb}$		
			Unirradiated, R_0	Irradiated, R_1	R_1/R_0
PbTe	n-type	Cadmium-shielded	-0.88	-4.3	4.9
		Unshielded	-1.1	-4.4	4.0
Bi ₂ Te ₃	n-type	Cadmium-shielded	-0.34	-0.19	0.56
		Unshielded	-0.40	-0.20	0.50
Bi ₂ Te ₃	p-type	Cadmium-shielded	+0.90	-0.45	-0.50
		Unshielded	+1.15	-0.22	-0.19

by these thermoelectric materials is due almost entirely to fast neutrons. From calculations, which were given above, the effects of transmutations appear to play a minor role. Only small differences are expected in the changes observed in the cadmium-shielded and unshielded samples containing initially doped material. The relatively large difference in the post-irradiation electrical resistivity of the shielded and unshielded n-type Bi₂Te₃ appears strange and is not understood. Perhaps one of the most striking changes given in Table 4 is the change of both shielded and unshielded p-type Bi₂Te₃ to n-type at room temperature.

For PbTe, which is known to be extrinsic at room temperature (i.e., current carriers predominantly of one sign only), the increase in Hall coefficient (see Table 6) caused by irradiation is directly interpretable as a corresponding decrease in carrier concentration. The measured decrease is consistent, with an error of only 20%, with the measured increase in the Seebeck coefficient as predicted by the theory of Pisarenko.* This theory gives a $\frac{k}{e} \ln \frac{1}{n}$ dependence of the Seebeck coefficient on carrier concentration, where n is the carrier concentration, k is the Boltzmann constant, and e is the electron charge. Thus, the decrease in carrier concentration could alone account for the large increase in the Seebeck coefficient of the n-type PbTe. Because p-type PbTe samples were broken, no Hall measurements could be made on them.

The Hall coefficient of Bi₂Te₃ is known to be markedly anisotropic, and differences in the crystal structure of the irradiated and unirradiated material are important. Hence, the interpretation of the ratio of

*A. F. Ioffe, Semiconductor Thermoelements and Thermoelectric Cooling (London: Infosearch, Ltd., 1957) (translated from the Russian version).

Hall coefficients in terms of the ratio of the concentration of the carriers above is not possible at this time.

Since the electrical conductivity is proportional to carrier concentration and mobility, it can be concluded for the n-type PbTe that the carrier mobility decreased by a factor of approximately 2.2 as a result of the irradiation. This follows because the electrical resistivity was increased by a factor of 10 (see Table 4), and the carrier concentration was decreased on the average by a factor 4.5 for the shielded and unshielded samples. It is presumed that the lowering of carrier concentration is due to trapping by the fast-neutron-induced defects.

High-Temperature Measurements

The measurements of resistivity and Seebeck coefficient for irradiated specimens as a function of temperature were compared with their unirradiated "sister" samples. At the beginning of this work no high-temperature facilities were available; hence, this is the only comparison that can be made. However, it is felt that differences in resistivity and Seebeck coefficient due to inhomogeneities of several samples cut from the same ingot are of the order of 10% or less. Therefore, it is reasoned that comparisons of irradiated and unirradiated "sister" samples are meaningful and can be made with due consideration for small differences caused by inhomogeneities.

n-Type Lead Telluride

The results of the first resistivity vs temperature run for the cadmium-shielded n-type PbTe are shown in Figure 10. No attempt to measure an annealing rate in the range of temperature 150 to 200°C was made. Within this temperature range the rapidly changing resistivity depends both on time and temperature in a complicated fashion. From these data one obtains a temperature of about 165°C for the onset of rapid annealing. The solid curve connecting the circular points represents the variation of resistivity with temperature for the unirradiated "sister" sample. It can be seen that the radiation damage to resistivity incurred by this sample was essentially completely annealed. These data are shown by solid circles, triangles, and squares connected by a dotted line. Such annealing phenomena are of common occurrence in semiconductors. It is suggested that a possible mechanism occurring is that the vacancy-interstitial pairs formed by fast neutrons are given sufficient recombination energy (via the increased lattice temperature) to return to their original lattice sites. A somewhat more elaborate experiment is needed to obtain explicitly the recombination energy.

It is to be assumed also that the radiation damage affecting the Seebeck emf annealed during this time also. After this annealing experiment was run, the Seebeck emf vs temperature was measured. These results

FIGURE 10. RESISTIVITY vs TEMPERATURE MEASUREMENTS FOR IRRADIATED (CADMIUM-SHIELDED) AND UNIRRADIATED n-TYPE LEAD TELLURIDE

are shown in Figure 11. It will be recalled that for this cadmium-shielded sample of n-type PbTe the room temperature Seebeck coefficient had increased by a factor 1.9. That this is no longer the case after annealing is evident from Figure 11. Consequently, one can conclude that both the resistivity and Seebeck coefficient are essentially completely annealed subsequent to such heat treatment.

The results for the unshielded n-type PbTe are shown in Figure 12, where the electrical resistivity is plotted versus temperature. In this experiment an attempt was made to measure the annealing rate. The temperature was raised slowly in order not to overshoot the annealing temperature ($\approx 165^\circ\text{C}$) measured for the cadmium-shielded sample (see Figure 10) of n-type PbTe. The temperature of the specimen was increased to a point where a reasonably fast annealing rate was detected. This temperature proved to be 155°C , and at this temperature the control circuit was put into operation. The temperature was kept at $155 \pm 1^\circ\text{C}$ for 4 hr and 10 min. The measurements of resistivity obtained during this time are

FIGURE 11. SEEBECK EMF vs TEMPERATURE MEASUREMENTS FOR IRRADIATED (CADMIUM-SHIELDED) AND UNIRRADIATED n-TYPE LEAD TELLURIDE AFTER ANNEALING

shown as crosses in Figure 12. The resistivity measurements shown by open circles in Figure 12 were taken 2 hr later.

Finally, after the sample had apparently completely annealed, a resistivity vs temperature run was made the following day. These measurements are shown by solid triangles in Figure 12. For temperatures greater than about 150°C the resistivity of the irradiated specimen appears significantly lower than its unirradiated "sister" sample. This is consistent

FIGURE 12. RESISTIVITY vs TEMPERATURE MEASUREMENTS FOR IRRADIATED (UNSHIELDED) AND UNIRRADIATED n-TYPE LEAD TELLURIDE

with the fact that the resistivity is lower the higher the concentration of doping agent becomes.* A valid conjecture then is that the radiation-induced iodine doping has qualitatively the same effect on the electrical properties as a chemical doping (with iodine) in the original melt of the PbTe crystal.

The results of the annealing rate experiment on the unshielded n-type PbTe sample are shown in Figure 13. It can be seen that there are at least two distinct rates of annealing of the radiation damage. A fairly rapid annealing takes place within about the first hour at 155°C, subsequent to which a much longer time (of the order of 8 to 10 hr) is required to anneal the damage completely. However, in view of the steep decrease of resistivity with temperature at about 175°C shown in Figure 10, it seems logical to conclude that this sample would have annealed in a much shorter time if the temperature had been increased to about 175°C. The resistivity of this sample after it had completely annealed is shown as a dotted line in Figure 13. The resistivity approaches this value asymptotically during the annealing process.

*Data furnished by R. W. Fritts, Minnesota Mining & Manufacturing Company, St. Paul, Minnesota.

FIGURE 13. A MEASUREMENT OF THE RATE OF ANNEALING OF RESISTIVITY WITH TIME FOR THE UNSHIELDED n-TYPE LEAD TELLURIDE

After these annealing runs were made on this unshielded sample of n-type PbTe, the Seebeck emf as a function of temperature was measured. These results are shown in Figure 14. It is recalled that prior to annealing the Seebeck coefficient (at 30°C) of this sample had exhibited an increase by a factor of 1.69 as a result of the irradiation. From Figure 14 it can be seen that this is no longer true and that apparently the Seebeck coefficient was completely annealed also. Again one is forced to make the fairly valid assumption that the Seebeck coefficient and resistivity were annealed simultaneously. However, there is not a large difference in the measured Seebeck emf for the irradiated and unirradiated samples. This is consistent with the fact that the Seebeck coefficient should depend less sensitively on the iodine concentration than the electrical resistivity, as measured elsewhere from iodine doping experiments.

On the basis of the experiments performed on n-type PbTe it can be concluded that for reactor flux-times of the order of 10^{20} nvt thermal and 10^{19} nvt fast:

1. The radiation damage is due almost entirely to fast neutrons,

FIGURE 14. SEEBECK EMF vs TEMPERATURE MEASUREMENTS FOR IRRADIATED (UNSHIELDED) AND UNIRRADIATED n-TYPE LEAD TELLURIDE AFTER ANNEALING

probably through interactions in which atoms are caused to be knocked out of their original positions in the lattice (Frenkle defects).

2. The radiation damage is essentially completely annealed by heat treatment at temperatures of 150 to 200°C.
3. The effects of transmutations are small and for all practical purposes are negligible in causing damage at these dosages.

4. Only very small changes in resistivity and Seebeck coefficient would have probably been observed if the samples were allowed to be irradiated at temperatures near 200°C. Clearly this last conclusion needs definitive experimental proof and is based on results* obtained with reactor-irradiated silicon.

n- and p-Type Bismuth Tellurides

The behavior of the electrical resistivity of the unshielded sample of n-type Bi_2Te_3 during annealing is shown in Figure 15. From this figure it can be deduced that most of the annealing takes place in the vicinity of 200°C and that the sample has completely annealed at about 300°C. However, the annealing takes place much more slowly with increasing temperature than was experienced with the n-type PbTe samples. For this sample no time rate of annealing experiment was attempted because of the unduly long time that would have been involved. Instead a procedure was adopted in which we sought to arrive at a temperature range from 150 to 250°C, where one observes the annealing clearly.

*Private communication from Dr. Nisenoff, Physics Department, Purdue University.

FIGURE 15. RESISTIVITY vs TEMPERATURE MEASUREMENTS FOR IRRADIATED (UNSHIELDED) AND UNIRRADIATED n-TYPE BISMUTH TELLURIDE

FIGURE 16. SEEBECK EMF vs TEMPERATURE MEASUREMENTS FOR IRRADIATED (UNSHIELDED) AND UNIRRADIATED n-TYPE BISMUTH TELLURIDE AFTER ANNEALING

The measurements of resistivity vs temperature after the sample had completely annealed are shown by solid triangles. In addition to the above the measurements for the unirradiated "sister" sample are depicted by open circles. The fairly large spread in the results for the unirradiated sample was unexpected, because of the reproducibility of similar data from the lead telluride. However, in two subsequent carefully performed runs on this same specimen similar results were obtained. Therefore, it is concluded that this spread is probably a peculiarity of

the sample designated as 202C (sample #8) which arises from radical changes in it at higher temperatures rather than from measurement errors only.

The Seebeck emf's measured for the irradiated (unshielded) and un-irradiated n-type Bi_2Te_3 as a function of temperature are shown in Figure 16 on the previous page. For this specimen the room temperature Seebeck coefficient (before annealing) had been measured to increase by about 16% as a result of the irradiation. Consequently no large effect on the Seebeck coefficient was anticipated for this sample after annealing. This is clearly evident in Figure 16; i.e., there are no detectable differences in the irradiated and unirradiated Seebeck emf's as a function of temperature.

The results of the annealing experiment to study the behavior of resistivity vs temperature for the cadmium-shielded n-type Bi_2Te_3 are shown in Figure 17 below. Here again one can conclude that most of the annealing takes place in the vicinity of 200°C, and again because of the time required no experiment on the rate of annealing was attempted. It appears that after annealing this sample exhibits a lower resistivity than its unirradiated "sister" sample. The difference (about 20% from a mean) is outside the experimental errors ($\approx 10\%$) and is probably due to inhomogeneities in the crystal. Inhomogeneities giving rise to resistivity

FIGURE 17. RESISTIVITY vs TEMPERATURE MEASUREMENTS FOR IRRADIATED (CADMIUM-SHIELDED) AND UNIRRADIATED n-TYPE BISMUTH TELLURIDE

FIGURE 18. SEEBECK EMF vs TEMPERATURE MEASUREMENTS FOR IRRADIATED (CADMIUM-SHIELDED) AND UNIRRADIATED n-TYPE BISMUTH TELLURIDE AFTER ANNEALING

differences of about 10% are entirely possible. One cannot invoke an argument regarding the increased iodine doping since the sample was cadmium-shielded.

The measurements of the Seebeck emf vs temperature for the irradiated (cadmium-shielded) and unirradiated "sister" sample of n-type Bi_2Te_3 are shown in Figure 18. It is recalled from the previous discussion (see

Table 4) that the measurement of the room temperature Seebeck coefficient (before annealing) for this sample had increased by only 4%, or to within an experimental uncertainty ($\sim 5\%$) had shown no significant changes as a result of the irradiation. In Figure 18 the Seebeck emf's for the irradiated and unirradiated samples are identical until a temperature of 150°C is reached. Above this temperature the irradiated sample exhibits a larger Seebeck emf with an increasing departure the higher the temperature. These differences (10% or less) are probably due in most part to inhomogeneities in the ingot.

The measurements of resistivity vs temperature for the irradiated (cadmium-shielded and unshielded) samples of p-type Bi_2Te_3 together with their unirradiated "sister" samples are shown in Figure 19 below. As was described in Table 4 the room temperature resistivity measurements for these particular irradiated samples had increased by factors of 1.2 ± 0.2 and 2.0 ± 0.2 , respectively, for the cadmium-shielded and unshielded p-type Bi_2Te_3 samples. It can be seen from the data that no experiment on the annealing rate was feasible for reasons mentioned previously. The results show that the irradiated, cadmium-shielded, p-type

FIGURE 19. RESISTIVITY vs TEMPERATURE MEASUREMENTS FOR IRRADIATED (BOTH WITH AND WITHOUT CADMIUM SHIELDS) P-TYPE BISMUTH TELLURIDE

FIGURE 20. SEEBECK EMF vs TEMPERATURE MEASUREMENTS FOR IRRADIATED (CADMIUM-SHIELDED) AND UNIRRADIATED p-TYPE BISMUTH TELLURIDE AFTER ANNEALING

Bi_2Te_3 sample shows the greatest unannealable change in electrical resistivity of all the samples measured. This result is not understood at present.

Once again it is recalled that both the cadmium-shielded and unshielded previously p-type Bi_2Te_3 samples exhibited n-type Seebeck coefficients at room temperature (before annealing) as a result of the irradiation. The preirradiation room temperature Seebeck coefficients were +171 and +192 $\mu\text{volts}/^\circ\text{C}$ for the cadmium-shielded and unshielded samples, while the corresponding postirradiation values were -140 and -202 $\mu\text{volts}/^\circ\text{C}$. This sign reversal was observed also in the room temperature Hall coefficient measurements given in Table 6. It might appear that, since the p-type Bi_2Te_3 was initially undoped, the radiation-induced iodine doping was sufficient to convert it to n-type. This is consistent with the fact that iodine added to the Bi_2Te_3 melt produces

FIGURE 21. SEEBECK EMF vs TEMPERATURE MEASUREMENTS FOR IRRADIATED (UNSHIELDED) AND UNIRRADIATED p-TYPE BISMUTH TELLURIDE AFTER ANNEALING

n-type material. However, this explanation is inconsistent with the fact that the cadmium-shielded sample of p-type Bi_2Te_3 was reversed in polarity also as a result of the irradiation.

After these samples had been heat-treated during the annealing process, the Seebeck emf's vs temperature were measured. The results of these measurements are shown in Figure 20 on the previous page for the cadmium-shielded sample and Figure 21 for the unshielded sample. The results for the corresponding unirradiated "sister" samples of p-type Bi_2Te_3 are included also. The measurements show that both samples of irradiated p-type Bi_2Te_3 which exhibited n-type behavior at room temperature subsequent to the irradiation returned to their original polarity following heat treatment. The similarity of the irradiation-induced changes in properties of the shielded and unshielded specimens

FIGURE 22. SEEBECK EMF vs TEMPERATURE MEASUREMENTS BEFORE AND AFTER HEAT TREATMENT OF IR-RADIATED (CADMIUM-SHIELDED) P-TYPE LEAD TELLURIDE. THE RESULTS FOR UNIRRADIATED P-TYPE LEAD TELLURIDE ARE INCLUDED.

and the fact that these changes were annealable both argue that some mechanism other than an iodine doping effect be invoked to explain the polarity reversal. It is suggested that again trapping of carriers by Frenkel defects may be responsible. The possibility that this material may be partially intrinsic at room temperature with unequal hole and electron mobilities makes such an explanation quite complex in the present instance. From the shape of the curves in Figures 20 and 21 it can be concluded that p-type Bi_2Te_3 (obtained from the Merck Company) begins to lose effectiveness at about 200°C. Moreover the Seebeck coefficient goes to zero in the range of temperatures from 200 to 250°C and becomes negative above this range.

p-Type Lead Telluride

Because both the cadmium-shielded and unshielded samples of p-type PbTe were broken inadvertently during the remote decapsulation process, it was possible to make only resistivity measurements at room temperature.

FIGURE 23. SEEBECK EMF VS TEMPERATURE MEASUREMENTS FOR IRRADIATED (UNSHIELDED) AND UNIRRADIATED P-TYPE LEAD TELLURIDE

These measurements yielded resistivity increases by factors of 25 ± 5 and 22 ± 5 for the cadmium-shielded and unshielded p-type PbTe samples. However, an attempt was made to measure the Seebeck emf's vs temperature on the broken pieces, which were now in the form of disks 1/4 in. in diameter and 1/4 in. or less in thickness. It can be seen from Figure 6b that the high temperature Seebeck apparatus is still capable of handling such small specimens.

The results of the Seebeck emf vs temperature for the irradiated (cadmium-shielded) and unirradiated ("sister" sample) p-type PbTe are shown in Figure 22 on the previous page. The measurement of the Seebeck coefficient at room temperature before annealing had shown an increase by a factor of 1.49 as a result of the irradiation (see Table 4). This is still the case if one compares the Seebeck emf at about 30°C before heat treatment (shown by crosses in Figure 22) with the corresponding

value of the unirradiated sample (shown by solid circles). After this initial run was completed, the sample was heated in a vacuum for 4 hr at 196°C, and another series of Seebeck emf vs temperature measurements was made. These measurements are shown by solid triangles in Figure 22. The results show that there still appears to be a significant difference in the magnitude of the measured emf for temperatures greater than about 200°C. The reasons for this pronounced difference are not understood since only a small portion of the difference is thought to be due to inhomogeneities in the crystal.

The results obtained from the measurements of Seebeck emf vs temperature for the irradiated (unshielded) and unirradiated ("sister" sample) p-type PbTe are shown in Figure 23 on the previous page. For this irradiated sample measurements of the Seebeck coefficient (before annealing) at room temperature yielded an increase by a factor of 1.74 as a result of

FIGURE 24. SEEBECK COEFFICIENTS vs TEMPERATURE FOR IRRADIATED (UNSHIELDED) AND UNIRRADIATED p- AND n-TYPE BISMUTH TELLURIDES

FIGURE 25. SEEBECK COEFFICIENTS vs TEMPERATURE FOR IRRADIATED (CADMIUM-SHIELDED) AND UNIRRADIATED p- AND n-TYPE BISMUTH TELLURIDES

the irradiation. This increase can still be observed in the results shown in Figure 23. Heat-treatment experiments on this sample will be run in a future experiment.

Presentation of Results in the Form of Seebeck Coefficients vs Temperature

The Seebeck coefficients as a function of temperature for irradiated (unshielded) and unirradiated p- and n-type Bi_2Te_3 are shown in Figure 24 on the previous page. As mentioned previously these results were extracted from the Seebeck emf vs temperature data by differentiation with an IBM-704 code. It can be seen that the Seebeck coefficient of the p-type Bi_2Te_3 goes to zero at temperatures in the range of 210 to 250°C. A comparison of these measurements with other results is not possible because the temperature dependence for the Seebeck coefficient and electrical resistivity for this material has not been obtained from other sources.

The corresponding Seebeck coefficient results for the irradiated (cadmium-shielded) and unirradiated p- and n-type Bi_2Te_3 are given in Figure 25 on the previous page. It is concluded that n-type samples yield results which for all practical purposes are identical with the unirradiated "sister" samples. For the p-materials there appear to be unannealed changes in the Seebeck coefficient for the cadmium-shielded Bi_2Te_3 and for the p-type PbTe.

FIGURE 26. SEEBECK COEFFICIENTS vs TEMPERATURE FOR IRRADIATED (CADMIUM-SHIELDED) AND UNIRRADIATED p- AND n-TYPE LEAD TELLURIDES

FIGURE 27. SEEBECK COEFFICIENTS vs TEMPERATURE FOR IRRADIATED (UNSHIELDED) AND UNIRRADIATED p- AND n-TYPE LEAD TELLURIDES

The Seebeck coefficients as a function of temperature for the unshielded and cadmium-shielded n- and p-type PbTe and for the corresponding unirradiated "sister" samples are shown in Figures 26 and 27, respectively.