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SEEBECK EFFECT IN MAGNESIUM SILICIDE

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SEEBECK EFFECT IN MAGNESIUM SILICIDE*

Marvin William Heller and G. C. Danielson

ABSTRACT

The Seebeck coefficient (thermoelectric power) has been measured from 7°K to 1000°K for both n-type and p-type single crystals of Mg_2Si . The room temperature carrier concentrations were as low as $3 \times 10^{16} \text{ cm}^{-3}$ for n-type samples and about $2 \times 10^{18} \text{ cm}^{-3}$ for the silver-doped, p-type samples. At low temperatures the magnitude of the Seebeck coefficient showed a pronounced maximum which is interpreted in terms of the phonon drag effect. The phonon contribution, S_p , was obtained from the measured Seebeck coefficient by subtracting off the electron diffusion term, S_e , which was calculated with the aid of the measured Hall coefficient. The magnitude of S_p was observed to be proportional to T^{-3} and to show the dependence on sample size and on carrier concentration predicted by the theory of C. Herring. At temperatures above 200°K, S_p was small compared to S_e . In the intrinsic temperature range (650°K to 1000°K) the Seebeck coefficients of the n-type samples were proportional to $1/T$ and implied a mobility ratio of about 3.5. Mass parameters of $m_n \approx 0.4 m_0$ and $m_p \approx 2 m_0$ were found to be consistent with the extrinsic Seebeck data as well as the intrinsic Hall and Seebeck data if optical-mode scattering predominated in the purer n-type samples and optical-mode scattering was comparable with ionized impurity scattering for the p-type samples at 300°K.

* This report is based on a Ph. D. thesis by Marvin W. Heller submitted November, 1960, to Iowa State University, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

I. INTRODUCTION

A. Seebeck Effect

In 1822-1823 Seebeck described in the Reports of the Prussian Academy of Sciences a phenomenon which he called "the magnetic polarization of metals and ores produced by a temperature difference". This phenomenon has since been definitely attributed to thermoelectric currents arising in a closed circuit made up of unlike conductors with the junctions at different temperatures. Unfortunately, Seebeck insisted on associating the effects of thermoelectric currents with magnetism. In spite of this misinterpretation of his own observations, Seebeck accumulated a large amount of information concerning the thermoelectric properties of many materials. Peltier's discovery of the liberation or absorption of heat at a junction of two dissimilar conductors through which an electric current is flowing followed in 1834. Finally, the Thomson effect, which is the liberation (or absorption) of heat (in addition to Joule heating) in a single conductor possessing both a temperature gradient and an electric current, was discovered in 1852.

It is interesting to note that, although Seebeck's discovery preceded Faraday's elucidation of the law of electromagnetic induction in 1831, electromagnetism and especially its practical applications have obscured the development of thermoelectric phenomena for many years. Recently, primarily due to the possibility of efficient thermoelectric conversion of heat to electrical energy, and cooling (or heating) using the Peltier effect,

considerable interest has been renewed in thermoelectric phenomena. Now, in some applications, thermoelectric devices may supplant electromagnetic devices. Recent interest in applications of thermoelectricity is due largely to the possibilities of converting heat energy directly to electrical energy offered by the thermoelectric properties of semiconductors.

The Seebeck coefficient (often called thermoelectric power) of semiconductors at low temperatures is especially interesting. Frederikse (11) in 1953 and Geballe and Hull (14) in 1954 reported magnitudes of the Seebeck coefficient of germanium which were anomalously large at low temperatures. Theories existing at that time were unable to account for these low temperature results. Herring (19) and Frederikse (11) independently have suggested that these anomalies are due to a dragging of the charge carriers by phonons streaming from hot to cold. This effect in metals was predicted by Gurevich (18) in 1945 and is sometimes called the Gurevich effect. Makinson (13) had also considered the carrying of electrons by phonons in the presence of a thermal gradient in connection with his study of thermal conduction in metals. The phonon drag effect results in a contribution (herein called the phonon Seebeck coefficient, S_p) in addition to the usual electronic term, S_e , which results from the tendency of charge carriers to diffuse from hot to cold.

B. Previous Studies of the Mg_2X Family of Compounds.

1. Seebeck effect

Mg_2Si is one member of the family of compounds Mg_2X , where X

represents the element silicon, germanium, tin or lead. The compounds have the antiferite structure having as a prototype CaF_2 . All of the compounds are semiconductors except Mg_2Pb which exhibits metallic behavior.

Boltaks and Zhuse (3) measured the Seebeck coefficient, as well as the Hall coefficient and electrical conductivity, of Mg_2Sn . Winkler (45) studied the Seebeck coefficient, Hall effect, and electrical conductivity of the complete series Mg_2Si , Mg_2Ge , Mg_2Sn , and Mg_2Pb . Winkler's samples were polycrystalline and he limited his analysis to the intrinsic temperature range. Busch and Winkler (7) reported Seebeck coefficient measurements of Mg_2Ge from 80°K to 1000°K in which the Seebeck coefficient of two n-type samples changed sign at about 150°K.

2. Other electrical properties

Nelson (34) investigated the optical and electrical properties of Mg_2Si and Mg_2Sn single crystals. Blunt, et al. (2) pulled single crystals of Mg_2Sn from the melt. Lawson, et al. (28) zone-refined Mg_2Sn in carbon boats. The latter two groups both studied electrical conductivity, Hall effect, optical absorption, and photoconductivity. Whitsett (42) measured the Hall coefficient and electrical conductivity of n-type Mg_2Si and n-type Mg_2Ge . Morris, et al. (33) studied Hall effect and electrical conductivity of single crystals of both n-type and p-type Mg_2Si ; Redin, et al. (36) made a parallel investigation of Mg_2Ge . Lynch, et al. (30) estimated the temperature dependence of the energy gap of Mg_2Si and Mg_2Ge from optical absorption measurements. Frederikse, et al. (12) measured the electrical

conductivity and Hall effect in Mg_2Sn from 2°K to 80°K. Zrudsky (46) measured the Hall coefficient and electrical conductivity of a Mg_2Si sample from 4°K to 300°K; he concluded that impurity band conduction predominated at temperatures below 50°K.

Table 1 summarizes the results of some recent studies of the Mg_2X compounds. In many cases, the inconsistency of the results obtained by different investigators is substantial.

C. Objectives of This Investigation

This investigation was undertaken in order to determine those fundamental properties of the charge carriers in Mg_2Si which can be obtained from a study of the Seebeck effect and its relation to the other semiconducting properties of Mg_2Si . Such knowledge of the properties of the charge carriers is necessary in order to understand the transport of heat and electricity in this type of semiconducting compound. It was desired to make measurements of the Seebeck coefficient over as wide a temperature range as possible and to interpret these results in terms of existing semiconductor theory. Since any theoretically predicted expression for the Seebeck coefficient will contain a number of parameters, Hall coefficient and electrical resistivity measurements were also desired. The behavior of the Seebeck coefficient at low temperatures was thought to be of special interest, since some semiconductors have exhibited striking phonon drag effects at low temperatures.

Table 1. Results of some studies of the Mg_2X family of compounds

Compound	Worker	Energy gap (ev) $E_G = E_{GO} + \beta T$ (ev)		Ratio of electron to hole mobility	Ratio of effective mass to electron rest mass		
		E_{GO}	$\beta \times 10^{-4}$ (ev/deg)		electrons	holes	
Mg_2Sn	Winkler (45)	0.36	-2.8	1.4	2.3	2.6	
	Nelson (34)	0.36	-3				
	Lawson, et al. (28)	0.34	+2.6	1.3	0.52	0.58	
	Blunt, et al. (2)	0.33	-3.5	1.3	1.2	1.3	
Mg_2Ge	Winkler (45)	0.74	-7.6	5.0	0.25	0.48	
	Whitsett (42)	0.63		2.5			
	Redin (36)	0.69		3.7	0.13	0.31	
	Lynch, et al. (30)		-6.5				
Mg_2Si	Winkler (45)	0.77	-6.4	5.7	0.36	0.72	
	Nelson (34)	0.79		4			
	Whitsett (42)	0.48		1.3	1.8	2.0	
	Morris (32)	0.78		4.8	0.46	0.87	
	Lynch, et al. (30)		-5				

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II. EXPERIMENTAL APPARATUS AND PROCEDURES

A. Preparation of Mg_2Si Samples

1. Preparation of the ingots

Single crystals of Mg_2Si were prepared from the purest magnesium and silicon commercially available and precautions were taken to prevent the introduction of additional impurities into the crystals during their preparation. Sublimed magnesium having a stated purity of 99.99 per cent was obtained from the Dow Chemical Company. The silicon used was Sylvania transistor grade with a room temperature resistivity of 40 ohm-cm. The magnesium was first cut into small pieces, then etched in dilute HNO_3 solution, and finally rinsed in distilled water before use. The silicon was not treated prior to use since it was free of surface contamination.

Because of the high reactivity of magnesium, some difficulty was encountered in finding a suitable crucible material. After several different materials were tried, graphite was selected. Even graphite is not entirely satisfactory, however, since it is wetted by Mg_2Si and is somewhat porous to the molten compound. The crucibles used consisted of two parts: an inner liner of spectroscopically pure graphite supplied by the National Carbon Company, and an outer screw-capped graphite cylinder of ordinary grade graphite. A drawing of the crucible is shown in Figure 1. After the crucible had been machined, both parts were rinsed in acetone and outgassed at 1200°C for twenty minutes at a pressure of 10^{-5} mm Hg to remove volatile impurities.

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SPECTROGRAPHICALLY
PURE GRAPHITE LINER

THERMOCOUPLE
WELLS

CAP

REGULAR GRADE
GRAPHITE

1 INCH

Figure 1. Crucible

7

At the melting point of the compound, 1090°C, magnesium has a very high vapor pressure; the boiling point is 1107°C. To reduce the loss of magnesium, the crystals were grown under an argon pressure of 20 pounds per square inch gauge pressure. The crystal growing chamber consisted of a zirconite tube (McDanel) with provisions for evacuation of the chamber to 10^{-5} mm Hg. Surrounding the tube was a cylindrical resistance furnace which could be raised at a controlled rate. The crucible was supported inside the chamber on a stainless steel rod which was joined through a copper rod to the water-cooled bottom plate of the chamber. This construction provided a thermal sink to encourage longitudinal rather than radial heat flow from the crucible.

The Bridgman (6) method of crystal growing was used. The essence of this method is that the melt is solidified by causing a solid-liquid interface to move slowly up from the lower tip to the top of the melt. Of the several crystallites which can nucleate in the lower tip of the melt, ideally only one predominates and determines the orientation of the bulk of the ingot. Because there were a large number of crystal growth variables which were difficult to control precisely, the crystal growth conditions were not systematically optimized. However, the following procedure seemed to give the best results:

- (a) Stoichiometric proportions of the constituents (two atoms of magnesium to one silicon) were used for most preparations and usually gave good compound in spite of the expected loss of magnesium. In fact, when one per cent extra magnesium was added, a magnesium - rich eutectic mixture resulted.

- (b) The constituents were heated rapidly to the melting point of the compound to minimize the loss of magnesium.
- (c) The melt was held at a temperature about 50° above the melting point for about 20 minutes to provide mixing.
- (d) A temperature gradient of 25°C per cm was produced by adjustment of the furnace height.
- (e) The furnace was raised and the power input was decreased in order to solidify the melt. The time for solidification was about thirty-five minutes.
- (f) After being solidified, the ingot was cooled to room temperature slowly (50°C per hour) to prevent fractures in the crystal.

All undoped crystals were n-type. To produce p-type crystals, approximately 0.02 per cent of high purity silver from the Johnson Matthey Company was added. In order to obtain p-type crystals with impurity concentrations comparable to those of undoped crystals, the number of silver atoms added should be only slightly greater than the number of charge carriers at room temperature in undoped crystals. However, due to lack of complete mixing of silver throughout the melt, it was necessary to add considerably more silver in order to obtain any extensive p-type regions. For this reason, the p-type crystals had impurity carrier concentrations of the order of 10^{18} cm^{-3} compared to 10^{16} for n-type. Sample 28B-5 was obtained from an ingot which had been doped with 0.003 per cent by weight of aluminum.

The cause of the n-type conductivity in undoped Mg_2Si crystals has

not been definitely established. Morris (32, page 83) gave arguments that the antiferite structure is stable against departure from stoichiometry and that the n-type conductivity of undoped Mg_2Si crystals is due to foreign impurities. The phase width of the compound Mg_2Si (see Figure 2) has been determined by Klemm and Westlinning (27) to be less than 0.1 atomic per cent. However, a very small deviation from stoichiometry, or a phase width of 0.01 atomic per cent, would be sufficient to account for the impurity concentrations (10^{16} per cm^3) in undoped crystals. Such a narrow phase width (0.005 per cent) for PbSe has been suggested by Goldberg and Mitchell (16). ✓

2. Selection and shaping of samples

The Mg_2Si ingots were usually bonded to the graphite inner crucible. Removal of the graphite resulted in the breaking up of the ingots into several pieces. The larger crystalline pieces were then examined for eutectic inclusions. In some cases, microscopic examination of polished surfaces was employed to determine the quality of the compound. The better ingots contained only widely separated small eutectic inclusions. Pieces found to be nearly eutectic-free were then cleaved to approximately the desired sample size. The final shaping of the small pieces into the form of rectangular parallelepipeds was done by grinding with first 400-mesh, then 600-mesh silicon carbide paper. The final size of the samples was about $1 \times 1.5 \times 7$ mm.

The sign of the charge carriers was determined from the sign of the thermal emf produced in a circuit consisting of a hot probe and a cold

Figure 2. Phase diagram of the magnesium-silicon system

probe placed in contact with the crystal. This probe method was especially useful for rapid identification of p-type regions in the Ag-doped crystals, which usually contained regions of both types of conductivity.

3. X-ray analysis

Usually polycrystalline structure in a sample could easily be detected by the observation of reflected light from a freshly ground surface, since such surfaces are actually made up of many minute cleavage planes. Samples showing polycrystalline structure were not used. After the measurements on the samples had been completed, back-reflection Laue pictures were taken of at least three different spots on each sample. The resulting pictures showed that all of the samples except 31B-2 were good single crystals. Pictures taken at four spots along the length of sample 31B-2 showed a double pattern. This double pattern indicated the presence of two orientations differing by approximately 4° ; careful optical observations later confirmed this interpretation. A multiple pattern, with the dots separated by less than one degree, was also observed at one isolated spot of sample 34B-3.

4. Sample uniformity

Since the resistivity was observed to vary considerably in the crystals, it was essential to check the uniformity of all the samples. The usual procedure was to check the uniformity of several samples from each ingot and then select the better ones for the measurements.

The uniformity test consisted of resistivity measurements at intervals of $1/40$ inch along both faces of each sample. The measurements were

made by means of sharpened tungsten probes 1.25 mm apart. The uniformity of each of the samples chosen for final measurements is shown in Figure 3.

5. Sample dimensions

The dimensions of the samples were measured using a Gaertner traveling microscope. Measurements of the width and thickness for each sample were made at two positions near the place where the potential probes for electrical measurements were to be located. The average of three determinations of each dimension: length, width, and thickness for each of the samples is shown in Table 2.

Table 2. Sample dimensions

Sample	Length (mm)	Width (mm)	Thickness (mm)
28B-5	5.4810	1.3270	0.9425
31B-2	6.1173	1.4992	1.0632
31B-3	6.6020	1.5000	1.0700
34B-3-I	6.6275	1.5674	1.1450
34B-3-II	6.6275	1.5674	0.8671
40B-4	7.0250	1.6883	1.1085
40B-8	5.9515	1.4495	1.0820

Figure 3. Sample uniformity

B. Method of Seebeck Coefficient Measurement

1. Definitions and sign convention

The Seebeck coefficient, often called thermoelectric power, is defined as the temperature derivative of the Seebeck emf, as shown in Figure 4 (a). The symbol S_A will be used to designate the absolute Seebeck coefficient of material A. $S_{AB} = S_A - S_B$ will be used to designate the Seebeck coefficient of material A relative to B. The sign convention illustrated in Figure 4(a) makes S_{XA} positive for hole conduction and negative for electron conduction, if X is a semiconductor and A is a reference metal such that $|S_X| > |S_A|$.

2. Thermoelectric circuit

In the thermoelectric circuit shown in Figure 4(b), two A-C thermocouples are attached to the ends of a sample of material X, under investigation. The sample ends are at temperatures T_1 and T_2 , respectively. The potential difference V_{XC} , with zero electric current flowing, can be found by integration of dV_{XC}/dT around the circuit from point 2 to point

1.

$$V_{XC} = \int_{2-1} \frac{dV_{XC}}{dT} dT + e_C, \quad (1)$$

or

$$V_{XC} = \int_{T_0}^{T_2} S_C dT + \int_{T_2}^{T_1} S_X dT + \int_{T_1}^{T_0} S_C dT + e_C, \quad (2)$$

$$S_{XA} = \lim_{T_2 - T_1 \rightarrow 0} \left(\frac{V_1 - V_2}{T_2 - T_1} \right) = \frac{dV_{XA}}{dT}$$

(a) Sign convention

(b) Thermoelectric circuit

Figure 4. Seebeck effect

or

$$V_{XC} = \int_{T_2}^{T_1} (S_X - S_C) dT + e_C. \quad (3) \quad \checkmark$$

The quantity e_C is the spurious voltage resulting primarily from inhomogeneities in the C wires. If $T_1 - T_2$ is small, S_X and S_C are essentially constant and $S_X - S_C = S_{XC}$ may be taken in front of the integral sign to give

$$V_{XC} = S_{XC} (T_1 - T_2) + e_C. \quad (4)$$

V_{XA} is obtained in a similar manner to be

$$V_{XA} = S_{XA} (T_1 - T_2) + e_A. \quad (5)$$

Now Equations 4 and 5 can be combined to give

$$V_{XC} = \left(\frac{S_{XC}}{S_{XA}} \right) V_{XA} - \left(\frac{S_{XC}}{S_{XA}} \right) e_A + e_C. \quad (6)$$

If $(T_1 - T_2)$ is varied over a range of at most a few degrees, only V_{XC} and V_{XA} change, and the slope

$$\frac{\Delta V_{XC}}{\Delta V_{XA}} = \frac{S_{XC}}{S_{XA}}. \quad (7) \quad \checkmark \checkmark$$

If Equation 7 is solved for S_X , the result is

$$S_X = \left(\frac{\Delta V_{XC}}{\Delta V_{XA}} S_A - S_C \right) / \left(\frac{\Delta V_{XC}}{\Delta V_{XA}} - 1 \right). \quad (8) \quad \checkmark \checkmark \checkmark$$

Thus if the slope $\Delta V_{XC} / \Delta V_{XA}$ is determined experimentally and S_C together with S_A are known, the absolute Seebeck coefficient of the sample, S_X , can be calculated. ✓

C. Apparatus and Procedures for Low Temperature Measurements

1. Sample holder and cryostat

The sample holder used for the Seebeck coefficient, Hall coefficient and electrical resistivity measurements in the temperature range 4°K to 300°K is shown in Figure 5. The holder was constructed mainly of bakelite except for the copper cap and electrodes. A cylindrical copper can (not shown in Figure 5) was made to slide tightly onto the copper cap. This can served to provide an isothermal region surrounding the sample.

The thermocouples shown in Figure 5 consisted of 5-mil gold plus 2.1 per cent cobalt wire and 5-mil copper wire. The gold alloy was obtained from the Sigmund Cohn Company. A 10-mil constantan wire was soldered to the upper electrode near the sample, thus providing a single copper-constantan thermocouple.

The drawing in Figure 5 indicates how several turns of the thermocouple wire were wound around and cemented with G. E. 7031 adhesive to the copper electrodes. Actually, the 5-mil tungsten lead wires from the potential probes were similarly anchored to the copper upper electrode. All the leads were also anchored thermally above the sample holder to a copper cylinder which was at the bath temperature.

Silk-covered 4-mil manganin heater wire was wound noninductively and cemented to each electrode. The leads to the heaters were of 10 mil manganin.

The copper lower electrode was constructed with a small mass so that its temperature could be changed readily by changing the power input

Figure 5. Low temperature sample holder

to the lower heater. A phosphor bronze spring and screw adjustment made possible the application of a variable spring pressure to hold the sample in place. The thickness of the cylindrical bakelite shell was made small near the top to reduce the thermal path between the two electrodes.

The potential probes were made of 18-mil tungsten wires which had been pointed in molten sodium nitrite. The probes were held in position by screws in such a way that spring action pressed the probes against the sample.

The cryostat shown in Figure 6 was used with liquid helium as the coolant from 4°K to 80°K and with liquid nitrogen as the coolant from 80°K to 300°K. The cryostat was about 5 feet long and 5 inches in diameter. The lower cylindrical portion, which enclosed the sample, was two inches in diameter to fit between the pole pieces of the magnet.

Six liters of liquid helium were required to fill the cryostat after it had been precooled with liquid nitrogen. A tantalum coil, not shown in the drawing in Figure 6, was suspended into the helium chamber; the superconducting transition at 4.3°K indicated when the cryostat was full.

The sample holder was suspended in the sample chamber of the cryostat by a thin-walled cupro-nickel tube. Radiation shields fastened at several places to this tube helped prevent heat influx to the sample region from the cryostat top. The leads were conducted out of the cryostat through Conax thermocouple glands. These thermocouple glands, using neoprene sealants, provided satisfactory vacuum seals which did not subject the lead wires to sharp temperature gradients. The minimizing

Figure 6. Cryostat

of temperature gradients along the lead wires was particularly important, since the gold-cobalt alloy was quite inhomogeneous in chemical composition. Sharp temperature gradients along the gold-cobalt wires would have caused large undesirable thermal emfs.

2. Mounting of samples

After the samples had been shaped, an air abrasive unit was used to make two small holes about 0.05 mm deep and about 2 mm apart in the sample sides. These holes served to seat the potential probes and prevent them from moving as a result of thermal expansion effects. It was necessary to measure the hole depths with a microscope in order to determine the separation of the Hall probes.

An ultrasonic soldering gun (Mullard) was used to tin the ends of the sample with zinc-tin solder. The thermocouple wires were joined by spot-welding, then soldered to the ends of the sample with pure indium solder. The sample was positioned in the holder with the slightly concave electrode faces pressing against the indium solder beads. Sufficient spring pressure was applied to cause the indium to deform, and thus to hold the sample firmly in place and establish good thermal contact between the sample and electrodes.

The potential probes were positioned with the points in the holes provided. The pressure produced by the spring action of the probes was adjusted to reduce the resistance of the probe-sample contact to a value less than 50 ohms. A Gaertner traveling microscope was used to measure the probe separation both before and after each data-taking run.

3. Procedures for taking data

Seebeck coefficient, Hall coefficient, and electrical resistivity measurements were made at many nearly constant temperatures in the range 4.2°K to 300°K. It was possible to change the temperature and level off at intervals of 2 to 3 degrees at the lower temperatures, and then at intervals progressively increased to 20° at room temperature. The steady-state temperatures below 20°K depended mainly on the pressure of exchange gas (helium); a pressure of about 0.01 mm Hg was used initially. To raise the temperature, a small amount of exchange gas was pumped out and the heater current increased. Near the end of a helium run (80°K) most of the exchange gas had been pumped out and a vacuum of 10^{-5} mm Hg was used from 80°K to 300°K. In this range the heater current was progressively increased in order to change the temperature. The temperature could be held constant during the measurement to about 0.5° at the lowest temperature; the control was somewhat better at higher temperatures.

The method used to measure the Seebeck coefficient, as described in Section II. B. 2., requires the determination of the quantity $\Delta V_{XC} / \Delta V_{XA}$, where C corresponds to copper and A corresponds to gold plus cobalt. If in Equations 4 and 5, the quantities e_C and e_A were zero (no spurious emfs due to inhomogenieties), then $\Delta V_{XC} / \Delta V_{XA}$ could be determined by measurement of V_{XC} and V_{XA} for only one temperature difference. However, whenever an alloy is used for one of the reference metals, e is usually several microvolts; e_A was about 40 microvolts at low temperatures,

using the gold plus cobalt wire. For these measurements, four different temperature differences in the range of zero to two degrees were produced by adjustment of the lower heater current. V_{XC} and V_{XA} were measured for each temperature gradient and the slope determined from a least-squares calculation. This method, which involves the measurement of V_{XC} and V_{XA} instead of the thermocouple voltages directly, was suggested by Shtenbek and Baranskii (40). The method has the advantage of reducing the required number of voltage measurements, if several different temperature gradients are used.

Since both V_{XC} and V_{XA} could not be measured simultaneously, alternate measurements were made a few seconds apart and an interpolation process was used to determine the values of the two voltages at a given time. An example of a series of voltage readings and the interpolated voltages is shown in Table 3; the interpolated values of V_{XC} and V_{XA} are shown graphically in Figure 7. The voltages were measured with a digital voltmeter (Kintel, model 456) preceded by a dc amplifier (Leeds and Northrup, model 9835 - B). The amplifier gain was 1000 which provided a basic sensitivity (smallest voltage change detectable) of 0.2 microvolts. This instrumental arrangement was chosen because successive V_{XC} and V_{XA} values could be measured rapidly, thus making the interpolation more accurate. The thermocouple wires were changed to copper in an ice bath after which all wires were of copper in order to minimize spurious emfs.

Hall effect and electrical resistivity measurements were made using a standard dc method; the probe arrangement, sample orientation, and

Table 3. Representative Seebeck data point, sample 34B-3, $T = 194.4^\circ\text{K}$

V_{XC} (microvolts)	V_{XA} (microvolts)	V_{XC} (microvolts)	V_{XA} (microvolts)
53.4			
	94.5	53.4	94.5
53.4			
	94.7		
53.6			
269.9			
	297.2		
269.2			
	296.9	269.2	296.9
269.2			
512.2			
	524.7		
512.4		512.4	524.8
	524.9		
758.0			
	755.0		
758.6			
	755.3		
758.2			
	755.0	758.2	755.0
758.2			
	755.1		

voltages are shown in Figure 8. The gold-cobalt thermocouple wires served as current leads; the current source was a 6-volt lead storage battery. The voltage across a standard resistor was measured in order to determine the sample current. A magnetic field of 10,000 gauss was produced by a Varian electromagnet, model V-4012A. The tapered pole pieces had faces 6 inches in diameter with a 2-inch separation. The voltages were measured with a Leeds and Northrup Type K-3 potentiometer in conjunction with an electronic

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Figure 7. Representative V_{XC} versus V_{XA} relation

Figure 8. Sample and probe orientation

null detector (both Kintel, model 204A and Leeds and Northrup, no. 9834 were used at different times). With this combination of instruments, potential measurements could be made to 1 microvolt or better, except at the lowest temperatures where increased sample resistance somewhat decreased the sensitivity.

The following sequence of potential measurements was used:

- V_T (thermocouple voltage)
- $V_S -$ (voltage across standard resistor, negative current)
- $V_{\rho-}$ (resistivity voltage with negative current)
- $V_{\rho+}$ (resistivity voltage with positive current)
- V_{HN+} (Hall voltage, magnetic field normal, current positive)
- V_{HN-} (Hall voltage, magnetic field normal, current negative)
- V_{HR-} (Hall voltage, magnetic field reversed, current negative)
- V_{HR+} (Hall voltage, magnetic field reversed, current positive)
- V_{S+} (voltage across standard resistor, positive current)
- V_T (thermocouple voltage)

The voltages for both sets of Hall and resistivity probes (V_{H1} , V_{H2} , $V_{\rho1}$, and $V_{\rho2}$ in Figure 8) were measured in the above sequence, which required about 15 minutes. Before these potential measurements were made, the temperature difference across the sample, as indicated by V_{XC} , was reduced to a near zero value. A representative series of actual potential measurements is given in Table 4.

The resistivity voltage was calculated by means of the formula

$$V = \frac{V_{\rho+} - V_{\rho-}}{2} \quad (9)$$

Table 4. Representative Hall and resistivity data point, sample 34B-3,

T = 81.8°K

Measurement	Probe set 1 (millivolts)	Probe set 2 (millivolts)
V_T	5.1215	5.1220
V_{S-}	5.0000	-
V_{ρ^-}	-4.7060	-3.8550
V_{ρ^+}	+4.3056	+3.6871
V_{HN+}	-2.9930	-2.1802
V_{HN-}	+3.0760	+2.0955
V_{HR-}	-2.2765	-2.9439
V_{HR+}	+2.3584	+2.8740
V_{S+}	4.9970	-
V_T	5.1220	5.1220

This combination of measured voltages eliminated spurious voltages which did not change sign rapidly with current reversal. The measured resistivity voltage always includes a thermoelectric contribution which results from the temperature difference produced by the Peltier effect. This contribution may establish itself very rapidly, depending on the heat capacity of the sample-electrode junctions. The error introduced from this contribution was minimized by rapid measurement of the voltages after current reversal; the resulting error was usually less than 1 per cent.

The current-dependence of the resistivity voltage was checked at several temperatures for most samples. The relationship obeyed Ohm's law in all cases except for the p-type samples at temperatures below 150°K. Because of this behavior, the low temperature resistivity data for the p-type samples were not considered reliable.

Following a method due to Lindberg (29), the measured Hall voltages were combined by means of the equation

$$V_H = \frac{V_{HN+} - V_{HN-} + V_{HR-} - V_{HR+}}{4} \quad (10)$$

This method eliminated all spurious voltages except that due to the Ettingshausen effect. The linearity of the Hall voltage with magnetic field was checked at several different temperatures for each sample. In all cases, for H up to 15 kilogauss, linearity to within a few per cent was observed.

Metal to semiconductor contacts were found to be rectifying for the p-type samples, especially at lower temperatures. The principal disadvantage of this rectifying property was the increased circuit resistance and consequent decrease in sensitivity of the voltage measurements. For example, the circuit resistance for n-type samples was about 100 ohms at 80°K; for p-type samples this resistance was about 1000 ohms. This resulted in a decrease in sensitivity by a factor of ten at 80°K and an even greater decrease at lower temperatures. Because of these difficulties, the Hall coefficient data for the p-type samples were not reliable at temperatures below 80°K.

4. Temperature measurement

The copper-constantan thermocouple was used to determine the temperature from 15°K to 300°K. Although the particular thermocouple used was not calibrated, several couples taken from the same spool had been calibrated over the range 80°K to 300°K. These various calibrations had a maximum emf variation which corresponded to 0.5 degree. One of these calibrations, Schirber (38), was used to determine the temperature from 15°K to 300°K. The thermocouple emfs were measured with a Type K-3 Leeds and Northrup potentiometer.

From 4°K to 15°K, the temperatures were determined with the gold plus 2.1 per cent cobalt versus copper thermocouple. This thermocouple has been described and a calibration given by Fuschillo (13). The couples used in this work were taken from a spool of gold plus 2.1 per cent cobalt wire from the Sigmund Cohn Company. Schirber (38) has made a calibration from 4°K to 300°K, based on couples from this spool. Apparently because of inhomogeneous composition, the emf of the couple used in this work was larger at 4°K than that given by Schirber's calibration. For this reason, it was necessary to establish a calibration point for this couple. This calibration point was obtained from a length of 2-mil tantalum wire wound on the upper electrode of the sample holder; the emf of the thermocouple was determined at the known superconducting transition temperature of tantalum (4.4°K). The temperature-emf relation from Schirber's calibration was then adjusted on the basis of this one calibration point.

5. Absolute Seebeck coefficients of gold + cobalt and copper

The determination of the absolute Seebeck coefficient of gold plus cobalt and copper was accomplished in two steps. First the Seebeck coefficient of gold plus cobalt relative to copper was taken directly from the calibration tables; the Seebeck coefficient of gold plus cobalt relative to copper equals Δemf divided by ΔT . Secondly the absolute Seebeck coefficient of copper was obtained from the work of Borelius (4). Borelius measured the Thomson coefficient of copper, σ_T , from 20°K to 300°K and obtained the Seebeck coefficient from the relation

$$S = \int_0^T \frac{\sigma_T}{T} dT. \quad (11)$$

Measurement of S_{Cu} relative to superconductors (whose Seebeck coefficients are zero) in the range 3.7°K to 7.2°K, and extrapolation of the measured Thomson coefficient from 7.2°K to 20°K, made possible the determination of $S_{\text{Cu}}(T)$ from 3.7°K to 300°K. A more recent tabulation of the absolute Seebeck coefficient of copper from 100°K to 300°K by Cusack and Kendall (9) was found to agree well with the work of Borelius.

D. Apparatus and Procedures for High-Temperature Measurements

1. Sample holder and furnace

The sample holder used for measurement of Hall coefficient, Seebeck coefficient, and electrical resistivity from 300°K to 1000°K is shown in Figure 9. The base of the holder was made of lava or talc (magnesium silicate) from the American Lava Corporation. This material is easily

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Figure 9. High temperature sample holder

machined before firing but, after firing, it becomes hard and possesses superior insulating properties at high temperatures. Two rectangular bosses having cylindrical holes housed the cylindrical electrodes and allowed the upper electrode to slide freely. The sample was held by pressure contact between the electrodes; the force was transmitted by a stainless steel rod from a spring located above the sample holder.

The electrodes were made of platinum. Chromel-constantan thermocouples (10 mil in diameter), after being butt-welded, were peened into small holes through the electrode ends. The thermocouple wires were thermally anchored to the electrodes with Saureisen cement as indicated in Figure 9. Small resistance heaters were imbedded in each of the electrodes to produce and control the temperature gradient in the sample. The potential probes were made of 20-mil tungsten wire. A platinum versus platinum plus 13 per cent rhodium thermocouple (10 mil diameter) was also spot-welded to each electrode and near the sample (for clarity these couples were not shown in Figure 9).

The sample holder was held on a stainless steel support in a rectangular vacuum furnace. This furnace consisted of two chambers: an inner sample chamber and an outer vacuum chamber containing the resistance furnace winding. The inner chamber was first evacuated to 10^{-5} mm Hg, then filled with argon to 25 pounds per square inch gauge pressure to minimize the loss of magnesium from the sample during the measurements. The leads were conducted out the top plate of the chamber through Conax thermocouple glands using teflon sealants.

2. Procedures for taking data

Temperature control in the range 300°K to 1000°K was accomplished with a Brown automatic controller. For a sensing element the temperature controller used a chromel-alumel thermocouple located in the furnace winding. The temperature was leveled off at intervals of 25° to 50° over the range 300°K to 1000°K. The temperature was held constant to about 2° while a set of measurements was being made.

The Seebeck coefficient in this range was measured by essentially the same procedure as that used for low temperature measurements. The basic method, outlined in Section II. B. 2., requires the measurement of the voltages V_{XK} and V_{XC} , where K now corresponds to constantan and C to chromel (see circuit of Figure 8). Because of the longer times required for steady state, only two temperature differences were produced in this case; four temperature differences were used for the measurements below room temperature. The voltages V_{XK} and V_{XC} were measured with a digital voltmeter preceded by a dc amplifier, as was done for the low temperature measurements. In addition, V_{XC} as a function of V_{XK} was traced directly by means of a Moseley X-Y plotter and two dc amplifiers. Thus two distinct determinations of the quantity $\Delta V_{XK} / \Delta V_{XC}$ were determined for each temperature.

The Hall coefficient and electrical resistivity were measured through use of the same procedures as described in Section II. C. 3.

3. Temperature measurement

A platinum versus platinum plus 13 per cent rhodium thermocouple

was used to determine the temperature for the range 300°K to 1000°K.

The emf-temperature relations for this couple were taken from the Leeds and Northrup Tables 077989, issue 2. This type of couple is generally considered to be reliable to better than 1 per cent in the range 300°K to 1000°K.

4. Absolute Seebeck coefficients of chromel and constantan

The Seebeck coefficient of chromel relative to platinum was obtained from an emf-temperature table supplied by the manufacturer of the chromel wire. Table E-271-CC, from the Hoskins Manufacturing Company, gave emf values to one microvolt from 273°K to 1573°K at 10-degree intervals.

The Seebeck coefficient of constantan relative to platinum was obtained from the work of Roeser and Dahl (37). Roeser gave a table of emfs of the couple constantan-platinum to one hundredth millivolt for every 50° from 73°K to 1275°K. The absolute Seebeck coefficient of platinum was obtained from Cusack and Kendall (9). Cusack has compiled absolute Seebeck coefficient results for several metals at high temperatures; in this compilation, he used the revised absolute scale due to Christian, et al. (8). Cusack estimates that the Seebeck coefficient results he tabulates should be accurate to about 5 per cent.

III. RESULTS

A. Experimental Results

1. Seebeck coefficient

The results of Seebeck coefficient measurements from 7°K to 1000°K on four n-type and two p-type samples of Mg₂Si are tabulated in the Appendix, Tables 8 through 14. Figure 10 shows the temperature dependence of the measured Seebeck coefficient of an n-type and a p-type sample of Mg₂Si from 7°K to 1000°K. The Seebeck coefficients for the two samples have opposite signs and large magnitudes at low temperatures. At higher temperatures, the Seebeck coefficients have the same sign and approach the same values in the intrinsic temperature range. The discontinuities in the curves at 300°K and the double values of S for sample 40B-8 from 300°K to 445 °K are explained in Section III. B. 2.

2. Hall coefficient and electrical resistivity

The Hall coefficient was calculated from the formula

$$R = \frac{t}{IH} V_H 10^8 \text{ (cm}^3\text{/coul) ,} \quad (12)$$

where V_H (volts) is obtained from Equation 10 and 10^8 is a units conversion factor. The symbols t , I , and H are identified in Section IV. A. The V_H determined for the two sets of Hall probes usually agreed within a few per cent; the average V_H was used in the calculations. The results of the Hall coefficient measurements are shown as a function of $1000/T$ in Figure 11. The graphs show the magnitude of the Hall coefficient: R is negative for the n-type samples (28B-5, 31B-2, 31B-3, and 34B-3)

Figure 10. Seebeck coefficient (S) of n-type (31B-3) and p-type (40B-8) Mg_2Si

throughout; R is positive for the p-type sample 40B-8 below $T = 600^\circ\text{K}$ and negative above this temperature.

The resistivity was calculated by means of the formula

$$\rho = \frac{wt}{sI} V_p \quad (\text{ohm-cm}), \quad (13)$$

where V_p (volts) is obtained from Equation 9; w and s are identified in Section IV. A. The resistivity voltages from the two sets of probes usually agreed quite well and the average was used in the calculation. The results of the resistivity measurements as a function of $1000/T$ are shown in Figure 11. The resistivity as well as Hall coefficient results are also tabulated in the Appendix, Tables 8 through 14. For reasons mentioned in Section II. C. 3., the resistivity data for the p-type samples 40B-4 and 40B-8 were not considered reliable for temperatures below 150°K ; also, the Hall data for the p-type samples were not reliable for temperatures below 80°K . Sample 40B-4 was broken during preparation for high temperature measurements; consequently, no measurements above 300°K could be made.

B. Errors

1. Low temperature Seebeck measurements

Errors in the Seebeck coefficient measurement could have been introduced by uncertainties in the absolute Seebeck coefficient of gold-cobalt and of copper, and by errors in the measurement of the Seebeck voltages.

The uncertainty in the absolute Seebeck coefficient of gold-cobalt was estimated from the uncertainties in the calibration emfs to be about

Figure 11. Hall coefficient (R) and electrical resistivity (ρ) of Mg_2Si

2 per cent at 7°K and less than 1 per cent at 300°K.

Borelius (4) estimated an error in the absolute Seebeck coefficient of copper of ± 0.1 microvolt per degree at room temperature. Even if the uncertainty in the absolute Seebeck coefficient of copper were as large as 5 per cent, it can be seen from Equation 8, that the resulting uncertainty in the Seebeck coefficient of Mg_2Si would be less than 1 per cent.

Because of the difference between the emfs of the gold plus cobalt versus copper thermocouples and those given by the calibration table (100 microvolts at 4°K), the possibility was considered that the particular couples used might have emf-temperature relations (Seebeck coefficients) which were different from those indicated by the calibration tables. An auxiliary experiment was performed using the copper-constantan thermocouple to determine the Seebeck coefficient of gold plus cobalt. The Seebeck coefficients of gold plus cobalt, measured in this manner, were found to agree with the values determined from the emf-temperature calibration to within 2 per cent from 15°K to 300°K. Since the copper-constantan thermocouples are known to be reliable, these results indicated that the Seebeck coefficients of gold plus cobalt, as determined from the calibration tables, were also reliable.

The uncertainty in the measured Seebeck voltage ratio, $\Delta V_{XC} / \Delta V_{XA}$, was found from the least-squares analysis to be about 4×10^{-4} at 10°K and about 3×10^{-4} at 300°K. Considering Equation 8 again, we see that the uncertainty in the Seebeck coefficient, S_X , is

$$\delta S_X = \frac{S_{CA}}{(1 - \frac{\Delta V_{XC}}{\Delta V_{XA}})^2} \times (\text{uncertainty in } \frac{\Delta V_{XC}}{\Delta V_{XA}}) \quad (14)$$

This expression gives an uncertainty of about 5 per cent at 10°K to 0.5 per cent at 300°K.

The above analysis assumed that the thermocouples at the ends of the sample were measuring accurately the temperature difference between the sample-metal junctions. Whether or not this assumption is valid is difficult to establish. However, several precautions, suggested by Geballe and Hull (14), were taken to prevent errors of this kind, and none of the following changes was observed to change the measured Seebeck coefficient more than three per cent:

- (a) The temperature difference was varied from a few hundredths to several degrees. Figure 7 shows a representative relationship of V_{XC} and V_{XA} .
- (b) The exchange gas pressure was varied from 10^{-5} mm to 1 mm Hg.
- (c) The bath temperature was changed from 4.2°K to 78°K and from 78°K to 300°K.
- (d) In the case of sample 34B-3 the sample was unsoldered, the contacts cleaned off, and the sample remounted.
- (e) The ratio of V_{XC} to the Seebeck voltage measured between the resistivity probes agreed well (10 per cent) with the ratio of the sample length to probe separation.

The increased resistivity of the purer n-type samples at low temperatures caused a decrease in the sensitivity of the voltage measurements,

and (see Section II. C. 3.) for the p-type samples the rectifying property of the semiconductor-metal contacts was especially serious. In view of the above considerations, the Seebeck coefficient measurements are believed to be reliable within 8 per cent at 10°K to 3 per cent at 300°K.

2. High temperature Seebeck measurements

The uncertainty of the Seebeck coefficient of chromel relative to platinum from 300°K to 1000°K was estimated to be 1 per cent or less. The Seebeck coefficient of constantan relative to platinum was found to be uncertain to about 2 per cent. The Seebeck coefficient of platinum has an uncertainty of 5 per cent, from Cusack and Kendall (9). Hence, the resulting uncertainties in the absolute Seebeck coefficients of chromel and constantan were about 5 per cent and 3 per cent, respectively. The absolute Seebeck coefficients of chromel and constantan were checked at several temperatures by the measurement of emfs in the chromel-platinum and constantan-platinum thermocouple circuits (this measurement was possible, since a platinum plus rhodium versus platinum thermocouple was spot-welded to each electrode). The Seebeck coefficients measured in this way agreed well with the values calculated from emf-temperature tables.

The question of whether the thermocouples were sensing the true temperature difference between the sample-electrode junctions was especially important with the arrangement used for the measurements above room temperature. With the arrangement shown in Figure 12, the thermocouples were not in actual contact with the sample. The following results were

obtained when checks on the reliability of the measurements were made.

The measured Seebeck coefficient of the sample:

- (a) was the same for a temperature difference from nearly zero to several degrees,
- (b) showed a slight increase in magnitude, 5 per cent, when the exchange gas pressure was varied from 10^{-4} mm Hg to 2 atmospheres,
- (c) showed an increase in magnitude as large as 8 per cent with increased force on the pressure contacts,
- (d) was for all samples at 300°K from 10 to 30 per cent lower in magnitude than the Seebeck coefficient measured with soldered contacts (see Figure 10).

The above results indicate that the thermocouples were not actually measuring the true temperature difference between the sample-electrode junctions, and that the thermal impedance of the pressure contacts was causing an error in the temperature difference sensed. To verify this conclusion, two samples were individually soldered in the high temperature sample holder and the Seebeck coefficient measured from 300°K to 450°K (the melting point of the solder). The resulting measured Seebeck coefficient joined up with the low temperature data very well for sample 34B-3 and reasonably well for sample 40B-8. Figure 10 shows the soldered-contact results for 40B-8 as the upper values of S from 300°K to 445°K. In Section 4 an analysis is given of the Seebeck measurement with thermal impedance at the junctions.

Figure 12. Thermoelectric circuit with thermal impedance
at sample-electrode junctions

3. Hall and resistivity measurements

Errors in the Hall coefficient and resistivity measurements could have been produced by errors in the determination of sample size, sample current, magnetic field strength, and Hall or resistivity voltages. In addition, the Ettingshausen effect could have introduced an error in the Hall measurement.

- (a) The sample dimensions were measured to approximately 3 per cent.
- (b) The sample current was measured to 0.1 per cent.
- (c) The magnetic field strength was known to 0.5 per cent.
- (d) The Hall voltage and resistivity voltage were measured to one microvolt, which represents an uncertainty of about 1 per cent. The uncertainty was larger in those cases where high circuit resistance decreased the sensitivity and where higher temperatures decreased the Hall voltage.

The Ettingshausen effect can cause an error in a Hall measurement by producing a transverse temperature difference which gives rise to a thermoelectric contribution to the voltage measured between the Hall probes. Morris (32, page 76), following a discussion by Johnson and Shipley (26), estimated the error produced by the Ettingshausen effect to be as large as 10 per cent at 1000°K, but less at lower temperatures. The total possible error might then be as large as 10 per cent for the resistivity and 15 per cent for the Hall coefficient.

4. Temperature measurement

The temperature measurements were believed to be accurate to 1 per cent or less at most temperatures. At the lowest temperatures, however, the sensitivity of the gold plus cobalt versus copper thermocouple was quite small; at 4°K, the sensitivity was 5 microvolts per degree. At these lowest temperatures the temperature measurement was probably uncertain to about 5 per cent.

5. Seebeck measurement with pressure contacts having thermal impedance

Figure 12 shows the thermoelectric circuit used for the Seebeck measurements from 300°K to 1000°K. A thermal impedance is assumed at the sample-electrode junctions. Since, during the measurement, heat will be flowing from the hotter electrode through the sample to the cooler electrode, a sharp change in the temperature gradient can occur at the junctions. Following the same procedure as that used for the case of no thermal junction impedance (Section II. B. 2.), we obtain the voltages V_{XC} and V_{XA} .

$$V_{XC} = S_{XC} (T_4 - T_1) + S_{PtX} [(T_2 - T_1) + (T_4 - T_3)] + e_C, \quad (15) \quad \checkmark \checkmark$$

$$V_{XK} = S_{XK} (T_4 - T_1) + S_{PtX} [(T_2 - T_1) + (T_4 - T_3)] + e_K. \quad (16) \quad \checkmark \checkmark$$

Now, if we assume that

$$(T_2 - T_1) + (T_4 - T_3) = \alpha (T_4 - T_1), \quad (17) \quad \checkmark$$

that is, that the sum of the temperature differences across the junctions is proportional to the temperature difference between the electrodes, then $(T_4 - T_1)$ can be eliminated between Equations 15 and 16 to give

$$V_{XC} = \frac{(S_{XC} + \alpha S_{PtX})}{(S_{XK} + \alpha S_{PtX})} V_{XK} - e_K \frac{(S_{XC} + \alpha S_{PtX})}{(S_{XK} + \alpha S_{PtX})} + e_C \quad (18)$$

There is still a linear relationship between V_{XC} and V_{XK} , as was the case for no thermal junction impedance. If $T_4 - T_1$ is varied through at most a few degrees, the expression for the slope, $\Delta V_{XC} / \Delta V_{XK}$, may be solved for S_X to give

$$S_X = \frac{1}{1 - \alpha} \left[\frac{\frac{\Delta V_{XC}}{\Delta V_{XK}} S_K - S_C}{\frac{\Delta V_{XC}}{\Delta V_{XK}} - 1} - \alpha S_{Pt} \right] \quad (19)$$

The first term in the square brackets is the measured Seebeck coefficient; the second term will usually be small ($S_{Pt} < 18 \mu$ v/deg from 300°K to 1000°K). Thus, the Seebeck coefficient measured with pressure contacts having thermal impedance may be too small in magnitude by a factor approximately equal to $1 - \alpha$.

6. Pressure contact correction

The results of the Seebeck measurements from 300°K to 1000°K indicated that indeed a pressure contact error was present. If the value of S measured with soldered contacts is assumed to be correct, then α may be calculated from Equation 19. The results of such calculations are: for sample 31B-3, $\alpha = 0.09$; 31B-2, $\alpha = 0.16$; 34B-3, $\alpha = 0.31$; 40B-8, $\alpha = 0.27$. If α had been constant during the course of the high temperature measurements, then Equation 19 would give the relationship of S (measured) to

$S_{X \rightarrow S}$ (true) and a correction could be applied from 300°K to 1000°K.

The results of the application of this correction for 31B-3 and 40B-8 are shown as the experimental points from 300°K to 1000°K in Figure 14; these may be compared with the uncorrected Seebeck coefficients in Figure 10.

IV. ANALYSIS AND INTERPRETATION

A. Symbols

The following symbols are used throughout this and the following sections:

b	Mobility ratio, μ_n/μ_p	✓✓
c	Sound velocity	(cm/sec)
E_b	Electron energy at the band edge	(ev)
E_G	Energy gap	(ev)
E_{GO}	Energy gap at $T = 0$	(ev)
e	Absolute electronic charge, 1.602×10^{-19} coul	
E	Energy	
$\mathcal{E}$	Electric field strength	(volts/cm) ✓
E_F	Fermi energy	(ev)
f	Electron distribution function	
H	Magnetic field strength	(gauss)
h	Planck's constant, 6.624×10^{-27} erg-sec
Electric current	(amperes)
k	Boltzmann's constant, 1.38×10^{-16} erg/deg(K)	
K	Wave number for electron or hole	(cm ⁻¹)
m_0	Rest mass of electron, hole, 9.107×10^{-28} gm	
m_n, m_p	Inertial effect mass of electron, hole	(gm)
$m^{(N)}$	Density of states effective mass	(gm)
n	Electron concentration in the conduction band	(cm ⁻³)
	(n may be used for charge carrier concentration if neither holes nor electrons are specifically indicated)	

N_D, N_A	Concentration of donors, acceptors	(cm^{-3})	
N_D^+, N_A^-	Concentration of ionized donors, acceptors	(cm^{-3})	
R	Hall coefficient	$(\text{cm}^3/\text{coul})$	
s	Separation of resistivity probes	(cm)	
S	Seebeck coefficient	$(\mu\text{v}/\text{deg})$	✓
S_e	Electronic contribution to Seebeck coefficient	$(\mu\text{v}/\text{deg})$	✓
S_p	Phonon contribution to Seebeck coefficient	$(\mu\text{v}/\text{deg})$	✓
t	Sample thickness	(cm)	
T	Temperature	(degrees Kelvin)	
v	Electron velocity	(cm/sec)	
V_H	Hall voltage	(volts)	
V_p	Resistivity voltage	(volts)	✓
α	Proportionality constant of pressure contact error		✓
β	Temperature coefficient of energy gap	$(\text{ev}/\text{deg K})$	✓
r	Ratio of Hall to drift mobility		✓
π	Peltier coefficient	(ev/coul)	✓
μ_n, μ_p	Mobility of electrons, holes	$(\text{cm}^2/\text{volt-sec})$	✓✓
ρ	Electrical resistivity	(ohm-cm)	✓
τ_p	Phonon relaxation time	(sec)	✓
τ_e	Electron relaxation time	(sec)	✓

B. Basic Relations

1. Seebeck coefficient

The Seebeck coefficient (or thermoelectric power) of a conductor can be obtained from a solution of the Boltzmann transport equation as shown by Fan (10, page 340). A similar method, following Herring (19), is to use the Kelvin relation, based on irreversible thermodynamics

$$S = \frac{\pi}{T} \quad (20)$$

The energy transported per charge carrier in isothermal conduction for a non-degenerate semiconductor with one sign of carrier predominating is (with the upper sign for electrons, the lower for holes)

$$-e\pi = (E_b - E_F) \pm |\Delta E_T|, \quad (21)$$

where $E_F - E_b$ is the potential energy and ΔE_T the average kinetic energy relative to the band edge. ΔE_T will be the order of kT while $E_F - E_b$ will ordinarily be somewhat larger.

An explicit expression for the two terms of Equation 21 must involve some knowledge of the band structure of the particular semiconductor. It is well known now that "spherical energy surfaces", the simple model in which the electron energy is a simple quadratic function of wave number, is not applicable to most semiconductors. Silicon and germanium, for example, are known to have much more complex energy surfaces. A model which does appear to be applicable to several semiconductors is the "many-valley" model of Herring (20). According to this model the locus of a given energy in K-space is a set of ellipsoids centered about band

edge points. The "many-valley" model may be applied without great complication. A "density of states" mass, $m^{(N)}$, is usually defined by the equation

$$N(E) = \frac{4\pi}{h^3} (2m^{(N)})^{3/2} |E - E_b|^{1/2}, \quad (22)$$

where $N(E) dE$ is the number of levels per unit volume in the range E to $E + dE$. This quantity $m^{(N)}$ equals the inertial effective mass, m_n , for the simple "spherical energy surface" model. If each surface of constant energy is a single ellipsoid, $m^{(N)}$ equals the geometric mean of the three principal effective masses, m_{ni} . If each surface is a set of N_v similar ellipsoids, $m^{(N)}$ is $N_v^{2/3}$ times the geometric mean of the principal effective masses.

The quantity $E_F - E_b$ can be evaluated by the usual formula, see Wilson (44, Chapter 5),

$$\frac{|E_F - E_b|}{kT} = \ln \frac{2(2\pi m^{(N)} kT)^{3/2}}{h^3 n}. \quad (23)$$

The term ΔE_T of Equation 21 can be evaluated if the usual assumption is made that a relaxation time $\tau(\vec{k})$ exists, and the first order perturbation f_1 of the electron distribution $f(\vec{k})$ by an electric field has been obtained. The result is, Blatt (1, page 273).

$$f_1 \propto \tau_e \vec{E} \cdot \vec{v}_K f_0. \quad (24)$$

The quantity ΔE_T then becomes

$$\Delta E_T = \frac{\int_0^\infty v^2 E^{3/2} \tau_e \frac{\partial f_0}{\partial E} dE}{\int_0^\infty v^2 E^{1/2} \tau_e \frac{\partial f_0}{\partial E} dE}. \quad (25)$$

When $\tau_e \propto (E - E_b)^q$ the quantity $\Delta E_T/kT$ can be evaluated to be $\Delta E_T/kT = 5/2 + q$. Thus the expression for the Seebeck coefficient obtained from Equations 20, 21, and 23 is

$$S = \mp \frac{k}{e} \left[\frac{|\Delta E_T|}{kT} - \ln \frac{nh^3}{2(2\pi m(N)kT)^{3/2}} \right], \quad (26)$$

where the upper sign is for electrons, and the lower sign is for holes.

For both holes and electrons present, Equation 26 may be generalized to

$$S = \frac{\sigma_n S_n + \sigma_h S_h}{\sigma_n + \sigma_h}, \quad (27)$$

where S_n , S_h are the Seebeck coefficients for electrons and holes separately, and σ_n , σ_h are the respective electrical conductivities.

2. Hall coefficient and resistivity

The Hall coefficient and resistivity of a non-degenerate semiconductor are

$$\rho = \frac{1}{ne\mu_n}, \quad (28)$$

$$\text{and } R = -\frac{Y}{ne}. \quad (29)$$

Analogous expressions can be written for p-type conduction. When both electrons and holes are present in significant numbers, Equations 28 and 29 become

$$\rho = \frac{1}{e(n\mu_n + p\mu_p)} \quad (30)$$

$$\text{and } R = -\frac{1}{e} \frac{(nY_n\mu_n^2 - pY_p\mu_p^2)}{(n\mu_n + p\mu_p)^2}. \quad (31)$$

Derivations for Equations 28 through 31 are given, for example, in Wilson (44, Chapter 8). The quantity γ is the ratio of Hall to drift mobility. For "spherical energy surfaces" and longitudinal acoustical-mode lattice scattering, $\gamma = \frac{3\pi}{8}$. For the "many-valley" model, Herring (20),

$$\gamma = \frac{\langle \Delta E \tau^2 \rangle \langle \Delta E \rangle}{\langle \Delta E \tau \rangle^2} \cdot \frac{3(\frac{1}{m_1 m_2} + \frac{1}{m_2 m_3} + \frac{1}{m_3 m_1})}{(\frac{1}{m_1} + \frac{1}{m_2} + \frac{1}{m_3})^2} \quad (32)$$

where the brackets $\langle \rangle$ denote an average over the distribution and $\Delta E = |E - E_b|$; m_1, m_2, m_3 are the inertial effective masses for the principal axes of the ellipsoids.

Another useful relation follows from the requirement of electrical neutrality

$$n + N_A^- = p + N_D^+ \quad (33)$$

The condition for non-degeneracy given by Shockley (39, page 242) is

$$T > 4.2(10)^{11} n^{2/3}$$

If n is taken from the measured Hall coefficients in this investigation, it can be seen that all the samples except 40B-8, 40B-4, and 28B-5 at $T < 40^\circ\text{K}$ were non-degenerate over essentially the complete temperature range of the measurements. Since no important results were obtained from the data of these three samples below 40°K and since the effects of the slight degeneracy would be small (Weiss (41)), only the non-degenerate case will be considered here.

C. Phonon Seebeck Coefficient - Extrinsic Range

1. Determination of electronic contribution, S_e

In Figure 13 a plot is shown of the Seebeck coefficients of the n-type samples of Mg_2Si from 7°K to 120°K. The Seebeck coefficients of the two purer samples, 31B-3 and 34B-3, do not appear to approach the origin at the lowest temperatures. This is unusual because the third law of thermodynamics requires that S approach zero as T approaches zero. Since at the lowest temperatures, the sample resistance is large and consequently the voltage measurements less accurate, experimental error may account for this behavior. Another possible explanation of this low temperature behavior is that the Seebeck coefficients are about to change sign. The facts that the Hall coefficients of these two samples decreased in magnitude at the lowest temperatures and actually changed sign for the case of 34B-3 at $T = 5^\circ K$ tend to confirm this hypothesis. A sign change in the Seebeck coefficient of silicon was observed by Geballe and Hull (15), who attributed the phenomenon to impurity band conduction. Reversals of the sign of the Hall coefficient at 5 - 10°K for Mg_2Sn were observed by Frederikse, et al. (12) who suggested surface conduction as the explanation.

The large increase in magnitude of the Seebeck coefficients at low temperatures, shown in Figure 13, is indicative of the phonon drag effect. In order to examine the phonon Seebeck coefficient, S_p , it is necessary to calculate the electronic contribution S_e .

Figure 13. Low temperature Seebeck coefficient (S) of n-type Mg_2Si

$$S_p = S_{\text{Meas.}} - S_e . \quad (34)$$

S_e can be calculated using Equation 26 and the number of charge carriers from the results of Hall measurements, Equation 29. The expression for S_e can be written

$$S_e = \mp \frac{k}{e} \left\{ r_n + 3/2 \ln \frac{m_n}{m_0} - \ln \gamma_n - \ln \left[\frac{h^3}{2e(2\pi m_0 k)^{3/2}} \right] + \ln (|R| T^{3/2}) \right\} , \quad (35)$$

where $r_n = \frac{\Delta E_T}{kT}$. The upper sign applies for electrons; the lower

sign and the subscripts, n, changed to p, apply for holes. In Equation 35 and subsequently, the symbol m_n or m_p is understood to be the density of states effective mass, $m^{(N)}$, if the "many-valley" model for a semiconductor is applicable; the energy band structure of Mg_2Si is not known.

If the quantity B_n given by

$$B_n = r_n + 3/2 \ln \frac{m_n}{m_0} - \ln \gamma_n , \quad r_n = \frac{\Delta E_T}{kT} \quad (36)$$

is independent of temperature, a plot of $S_{\text{Meas.}}$ versus $\ln (|R| T^{3/2})$ will be linear with a slope of $(\mp \frac{k}{e})$ when Equation 35 adequately represents the Seebeck coefficient. Plots of $\ln (|R| T^{3/2})$ versus S were made; the results indicated that Equation 35 represented the data reasonably well in the range from 200°K to 300°K. Apparently the phonon contribution S_p was quite small in this range and at higher temperatures. Since the

exact effective masses and the scattering mechanisms were not known, it was necessary to adjust the quantity B_n as a parameter. In this analysis not only the effective masses, but also r_n and r_p as well as Υ were considered independent of temperature. ✓

The best fit of Equation 35 to the measured Seebeck coefficients for the various samples resulted in the following: $B_n = 1.22$ for 31B-3; $B_n = 1.17$ for 31B-2; $B_n = 1.03$ for 34B-3; $B_n = 1.63$ for 28B-5; $B_p = 4.17$ for 40B-8; and $B_p = 3.87$ for 40B-4. The implications of these values will be discussed in Section IV. D. 5.

The variation of B_n for the similar n-type samples 31B-3, 31B-2 and 34B-3 is probably not due to variations in m_n/m_0 or r_n but instead to sample inhomogeneity or errors in the dimensions used for the calculation of R . It should be pointed out that the Hall coefficient was determined for the central portion of the sample (the region between the Hall probes) while the Seebeck coefficient was determined across the whole sample. The fact that the more impure n-type sample, 28B-5, gave a value of B_n somewhat larger than those obtained for the other n-type samples is probably due to the influence of ionized impurity scattering in 28B-5 (Section IV. D. 5.).

A plot of S_e is shown for samples 31B-3 and 40B-8 in Figure 14. The curve for 31B-3 from 10°K to 420°K and the curve for 40B-8 from 50°K to 480°K were calculated from Equation 35. The calculation of the curves for higher temperatures is discussed in Section IV. D. 1.

Figure 14. Calculated Seebeck coefficient (curves) compared with experiment (points)

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The increase at 20°K in the magnitude of the calculated Seebeck coefficient for 31B-3 is the result of the depletion of the number of charge carriers when kT becomes comparable to the donor ionization energy. This indication of the donor ionization energy (2×10^{-3} ev) may be compared to the value 10^{-2} ev which was estimated from the slope of a plot of $\ln RT^{3/4}$ versus $1/T$ at low temperatures for sample 31B-3 as well as for 31B-2 and 34B-3 (Wilson (44), page 115).

2. Phonon Seebeck coefficient

The resulting phonon Seebeck coefficients determined from Equations 34 and 35 are shown as a function of T (log-log scale) in Figure 15. The samples 31B-2, 31B-3, and 34B-3 all show nearly the same temperature dependence; $|S_p|$ is proportional to T^{-3} for the purest sample, 34B-3. The value of $|S_p|$ decreases at lower temperatures where boundary scattering tends to restore the equilibrium of the phonon distribution. The resulting S_p for the p-type samples 40B-4 and 40B-8 showed considerable scatter because of the scatter in the Hall data at low temperatures. ✓ ✓

D. Transition and Intrinsic Ranges

1. Seebeck coefficient for two types of current carriers

When both holes and electrons are present in significant numbers, the Seebeck coefficient, given by Equations 27, 35, and 36, can be written

$$S = \frac{k}{e} \left(\frac{1}{nb + p} \right) \left[-nb(B_n - \ln \frac{n}{\gamma_n T^{3/2}}) + p(B_p - \ln \frac{p}{\gamma_p T^{3/2}}) \right] \quad \checkmark$$

Figure 15. Phonon Seebeck coefficient for n-type Mg_2Si
(log-log scale, dotted line has slope -3)

$$-(p - nb) \ln \frac{h^3}{2(2\pi m_o k)^{3/2}} \quad (37)$$

where S now represents the total Seebeck coefficient, that is, we assume $|S_p| \ll |S_e|$. The values of n and p can be obtained from the measured values of the Hall coefficient, R , and the equations of charge conservation, Equations 31 and 33, provided $N_D^+ - N_A^-$ is known. The latter quantity can be taken from an extrapolation of the extrinsic Hall coefficient before the intrinsic fall-off; see Figure 11. The equation is

$$N_D^+ - N_A^- = - \frac{\gamma}{R e} \quad (38)$$

The quantities B_n and B_p , and b are in general temperature dependent, but the principal temperature dependence in Equation 37 is due to n and p . Thus, it is possible to test the consistency of Hall and Seebeck coefficient measurements and the applicability of Equation 37 by using for B_n and B_p , the results of Section IV. C. 1., and the value $b = 3.6$ determined in Section IV. D. 3. This calculation was carried out (with the assumption $\gamma_n = \gamma_p$) for samples 31B-2, 31B-3, 34B-3, and 40B-8.

The resulting calculated Seebeck coefficients from 400°K to 1000°K for 31B-3 and 40B-8 are shown in Figure 14; the measured Seebeck coefficients are shown for comparison. The following values of the parameters, B , (see Section IV. C. 1.) were used: for 31B-3, $B_n = 1.22$ found for this particular sample, $B_p = 4.0$ the average of the values found

for the p-type samples; for 40B-8, $B_p = 4.17$ found for this particular sample, and $B_n = 1.14$ the average of the values found for the three purest n-type samples. The fact that the curves in Figure 14 tend to be slightly more positive at higher temperatures than the experimental points, indicates that in Equation 37, for sample 31B-3, B_p was chosen too large and that for sample 40B-8, B_n was chosen too small. This interpretation is supported by the results of Section IV. D. 5.: a large amount of impurity scattering present in sample 40B-8 would suggest $r_n \approx 3.2$ and consequently $B_n > 1.14$; only a small amount of impurity scattering in sample 31B-3 would suggest $r_p \approx 2.5$ and, consequently, $B_p < 4.17$. ✓ ✓

In view of the above considerations, the agreement between the calculated and experimental Seebeck coefficients in Figure 14 seems reasonable and thus tends to justify the choice of the values for the parameters, B_n and B_p , used for the determination of S_e and S_p in Sections IV. C. 1. and 2.

2. Energy gap

In the intrinsic temperature range, when $n = p = n_i$, the Hall coefficient is given by Equation 31. If E_F is eliminated between Equation 23 solved for n and a similar expression for p , and then the resulting expression for n_i substituted into Equation 31, the result for R can be written:

$$\ln |R| T^{3/2} = \ln \gamma - 3/4 \ln m_n m_p + \ln \left(\frac{b-1}{b+1} \right) - \ln 2e \left(\frac{2\pi k}{h^2} \right)^{3/2} + \frac{E_{GO}}{2kT} + \frac{\beta}{2k} \quad (39)$$

where $E_G = E_{GO} + \beta T$ and γ_n has been set equal to γ_p . If it is assumed that the principal temperature dependence in Equation 39 is contained in $E_{GO}/2kT$, then the slope of a plot of $\ln |R| T^{3/2}$ versus $1/T$ will yield the energy gap at $T = 0$, E_{GO} . Figure 16 shows a plot of $\ln |R| T^{3/2}$ versus $1000/T$ for three n-type samples. From the slopes of these curves, the average value, $E_{GO} = 0.80$ was obtained, in good agreement with Morris, et al. (33). The intercept of $\ln |R| T^{3/2}$ versus $1/T$ is also of interest, if the values of β and b are known. The mobility ratio $b = 3.6$ is determined in Section IV. D. 3. and $\beta = -5 \times 10^{-4}$ ev/deg is known approximately from optical absorption work, Lynch, et al. (30). The average intercept in Figure 16 gives the result

$$\ln \left(\frac{m_n m_p}{m_o^2} \right) = 4/3 \ln \gamma = -0.171 \quad (40)$$

This result will be discussed in Section IV. D. 5.

3. Mobility ratio

The Seebeck coefficient in the intrinsic temperature range is obtained from Equations 31, 37 and 39 with $n = p$ and $\gamma_n = \gamma_p$.

Figure 16. $|R|T^{3/2}$ versus $1000/T$ for three n-type Mg_2Si samples

$$S = -\frac{k}{e} \left[\left(\frac{b-1}{b+1} \right) \left(\frac{E_{GO}}{2kT} + \frac{\beta}{2k} \right) + \frac{1}{(b+1)} (br_n - r_p) + \frac{3}{4} \ln \frac{m_n}{m_p} \right]. \quad (41)$$

Again, if the temperature dependence of b , r_n , r_p are negligible and the correct temperature dependence of the energy gap is expressed as $E_G = E_{GO} + \beta T$, then a plot of S versus $1/T$ will be linear. Figure 17 shows a plot of S (uncorrected for pressure contacts) versus $1000/T$ for three n-type Mg_2Si samples. Only for 31B-3 is the behavior linear over an extended temperature range; however, all three samples show a common slope at higher temperatures. It appears that the pressure contacts for 31B-2 and 34B-3 were not stable with temperature and (see Section III. B. 5.) decreased somewhat at about $800^\circ K$, then stabilized at the highest temperatures. The pressure contacts for sample 31B-3 were apparently reasonably stable, as evidenced by the extended linear region of S versus $1000/T$; therefore, the slope for this sample was used to obtain b . Figure 18 shows in greater detail S versus $1000/T$ for 31B-3, showing the uncorrected S as well as the S corrected for pressure contact error. (Section III. B. 6.) It can be seen that both the corrected and uncorrected curves are linear, which is expected, since as mentioned in Section III. B. 5., S (measured) is nearly proportional to S (true). The slope of the uncorrected data implies $b \approx 3.0$ while the corrected data implies $b = 3.6$.

Figure 17. Seebeck coefficient of n-type Mg_2Si in the transition and intrinsic ranges

Figure 18. Effect of pressure contact correction
in the intrinsic range

Further evidence that the mobility ratio is about 3.5 was obtained from the results of some preliminary measurements. Only the Seebeck coefficient was measured, using a different apparatus but the same method as that described in Section II. C. 3. The results for the three purest samples are shown in Figure 19. A slope of S versus $1000/T$ of -200 mv gives $b = 3$; however, since these data were also taken with $\textcircled{Q}$ pressure contacts, it is possible that thermal junction impedance affected the $\textcircled{Q}$ measurements and that $b > 3$. Unfortunately, the value of α for these data could not be determined, since no measurements were made with soldered contacts.

With the value of b known, together with $\beta = -5 \times 10^{-4}$ ev/deg and $E_{GO} = \textcircled{Q}.80$ ev, the intercept of S versus $1000/T$, Figure 18, gives

$$\ln \frac{m_n}{m_p} = 0.540 + 0.289 r_p - 1.042 r_n . \quad (42)$$

The result is discussed in Section IV. D. 5. It can be seen in Figure 18 that the pressure contact correction has very little effect on the intercept.

4. Hall mobility

The Hall mobility, defined as R/ρ , is shown for all the samples of Mg_2Si in Figure 20. The temperature dependence of the R/ρ is seen to be near $T^{-5/2}$ for the n-type samples from 200°K to 1000°K . For the p-type samples the temperature dependence of R/ρ is closer to $T^{-3/2}$ at moderate temperatures. The comparison of the temperature dependences

Figure 19. Seebeck coefficient of n-type Mg_2Si (Preliminary measurements)

of $(R/\rho)_n$ and $(R/\rho)_p$ is not conclusive, however, due to the difference in carrier concentrations of the n-and p-type samples. Sample 28B-5 which, like 40B-8 and 40B-4, was quite impure also shows a temperature dependence less than $T^{-5/2}$ at moderate temperatures. At temperatures below 60°K, R/ρ shows a positive slope indicative of ionized impurity scattering. No detailed analysis of the Hall mobilities was attempted in this investigation.

Morris, et al. (33) observed a similar temperature dependence for the Hall mobility of Mg_2Si . Morris was able to obtain a reasonable fit to the experimental mobility at low temperatures using a combination of optical mode and ionized impurity scattering, requiring a dielectric constant of $\epsilon = 18$. At high temperatures a reasonable fit was obtained with a combination of either optical-mode or acoustical-mode with electron-hole scattering, but this fit required the unreasonably small value $\epsilon = 3$. It was necessary to invoke electron-hole scattering in order to produce a temperature dependence as large as $T^{-5/2}$. However, Herring (20) has shown that temperature dependences of mobility greater than $T^{-3/2}$ can result from intervalley acoustical-mode scattering.

5. Effective masses

The results of Section IV. C. 1. from Seebeck coefficient data in the extrinsic temperature range gave the following average values for B_n is the average result for the three purer n-type samples 34B-3, 31B-3 and 31B-2):

Figure 20. Hall mobility, R/ρ , versus temperature (log-log scale)

$$\bar{B}_n = r_n + 3/2 \ln m_n/m_o - \ln \gamma_n = 1.14 , \quad (43) \quad \checkmark$$

$$\bar{B}_p = r_p + 3/2 \ln m_p/m_o - \ln \gamma_p = 4.0 . \quad (44)$$

Thus the effective masses, m_n/m_o and m_p/m_o , could be determined if the type of scattering were known and a model assumed for the $E(\vec{K})$ relationship. Alternatively, if the effective masses were known, deductions could be made concerning the scattering mechanisms. Furthermore, Equations 40 and 42, based on data in the intrinsic temperature range, could be used to estimate results for comparison with the consequences of Equations 43 and 44. Unfortunately, however, as was pointed out in the preceding section, the dominant scattering mechanisms for Mg_2Si have not been definitely established ~~nor~~ have the effective masses been accurately determined. For these reasons, precise determinations of the effective masses or scattering mechanisms cannot be made. However, it is possible to draw some tentative conclusions concerning the scattering mechanisms, then, on the basis of these conclusions, to determine values for the effective masses.

The values of r and γ for different types of scattering, Johnson (25), assuming $E \propto K^2$, are given in Table 5. If the same scattering mechanism is assumed dominant from 300°K through 700°K (which is not unreasonable, since R/ρ for the purer n-type samples was nearly proportional to $T^{-5/2}$ throughout this range, Figure 20), Equations 43 and 44 can be combined with either Equation 40 or 42 to give an estimate of r . ✓
✓
✓

Table 5. Values of r and γ for various scattering mechanisms

Type of scattering	$\Delta E_T/kT = r$	γ
Intra-valley, longitudinal acoustical-mode	2	1.178
Inter-valley, longitudinal acoustical-mode	$r \gtrsim 2$	$\gamma \gtrsim 1.178$
Optical-mode	$2 < r < 3$	1.1
Ionized impurity	4	1.9
Electron-hole	4	1.9

With $\gamma_n = \gamma_p$ and $r_n = r_p$, Equations 43 and 44 combined with Equation 40 give the value $r = 2.7$; Equations 43 and 44 combined with Equation 42 give $r = 3.2$. These values imply that optical-mode scattering is important in Mg_2Si (see Table 5) which is in agreement with the conclusions of Morris, et al. (33).

The effective masses can now be calculated from Equations 43 and 44 and also estimated from Equations 40 and 42 with the assumption that optical-mode scattering predominated except in the case of the more impure samples in which ionized impurity scattering may have been appreciable. Howarth and Sondheimer (22) tabulated r as a function of $h\nu/kT$ for optical-mode scattering, where ν is the frequency of the optic mode. With $h\nu/k \approx 400^\circ K$ (Morris, et al. (33)), Howarth's results suggested that $r \approx 2.5$ at $300^\circ K$ and that $r \approx 2.8$ at $700^\circ K$ for Mg_2Si . Equations 40 and 42 were obtained from the data of the purer n-type samples in the intrinsic range,

hence the values $r_n = r_p = 2.8$ and $\gamma_n = \gamma_p = 1.1$ (Table 5) were used to obtain $m_n \cong 0.45 m_0$ and $m_p \cong 2.1 m_0$. Equations 43 and 44 were obtained from data in the extrinsic range; thus from Table 5, the values of r and γ will be $2.5 < r < 4$ and $1.1 < \gamma < 1.9$, the exact values depending on the relative importance of optical-mode and ionized impurity scattering. The mobility formulas of Morris, et al. (33) were used to estimate the relative importance of optical-mode and ionized impurity scattering in the samples of this investigation. Equation 43 was determined from the data of n-type samples with $n \cong 5 \times 10^{16} \text{ cm}^{-3}$ at 300°K ; for such samples, the ratio of ionized impurity mobility to optical-mode mobility was found to be, $\mu_I/\mu_O \cong 30$. From this result, it was concluded that optical-mode scattering predominated at 300°K ; hence, $r_n = 2.5$ and $\gamma_n = 1.1$ were used in Equation 43 to obtain $m_n = 0.43 m_0$. For Equation 44, based on the data of two p-type samples with $p = 2 \times 10^{18} \text{ cm}^{-3}$ at 300°K , $\mu_I/\mu_O \cong 1$ suggested that ionized impurity scattering and optical-mode scattering were comparable and hence that $r_p \cong 3.2$ and $\gamma_p \cong 1.5$. When these values for r_p and γ_p were substituted in Equation 44, $m_p = 2.23 m_0$ was obtained. Table 6 summarizes the results of the above effective mass calculations; the results of other possible assumptions for r and γ are included in parentheses. It should be pointed out that (see Tables 5 and 6) reasonably consistent values of the effective masses ($m_n = 0.6 m_0$ and $m_p \cong 2 m_0$) may be obtained from the extrinsic and intrinsic data with the assumption that acoustical-mode scattering predominated for Equations 40, 42, and 43, but that a large amount of ionized

Table 6. Summary of effective mass calculations

Equations	Basis for equations	Assumptions		Results	
		r	γ	m_n/m_o	m_p/m_o
40	Intrinsic Hall and	2.8	1.1	0.45	2.1
42	Seebeck data of n-type	(2.0)	(1.178)	(0.63)	(1.7)
	samples ($n \approx 5 \times 10^{16}$	(4.0)	(1.9)	(0.41)	(4.9)
	cm^{-3} at 300°K)				
43	Extrinsic Seebeck data	2.5	1.1	0.43	
	of n-type samples ($n \approx$	(2.0)	(1.178)	(0.63)	
	$5 \times 10^{16} \text{ cm}^{-3}$ at 300°K)				
44	Extrinsic Seebeck data	3.2	1.5		2.23
	of p-type samples ($n =$	(2.0)	(1.178)		(4.23)
	$2 \times 10^{18} \text{ cm}^{-3}$ at 300°K)	(3.5)	(1.7)		(2.0)

impurity scattering was present for Equation 44. However, this latter interpretation is not in agreement with the indication of experimental Hall mobility data (Morris, et al. (33)) that optical mode scattering is important in Mg_2Si .

V. DISCUSSION

A. Phonon Seebeck Coefficient

1. Temperature dependence of S_p

The most complete theoretical analysis of the phonon contribution to the Seebeck coefficient has been given by Herring (19); his analysis will be used to compare the results of this investigation with theory. Herring, using what he calls the " π approach", establishes a proportionality between the energy flux and the phonon crystal momentum in an isothermal specimen carrying an electric current. The contribution to the Seebeck coefficient is then found from $S_p = \pi/T$. An equivalent approach used by Frederikse (11), called the "S approach", is to consider the electric field resulting from the preferential phonon scattering of the charge carriers in a specimen with a temperature gradient.

Herring's simplified result is

$$S_p = \frac{m \bar{c}^2 \tau_p}{e T \tau_e} f \quad (45)$$

where f is the fraction of the crystal momentum lost by electrons which is delivered to longitudinal-mode lattice vibrations ($f = 1$ in the absence of impurity scattering if the transverse modes are negligible). Consideration of the magnitudes of the quantities in Equation 45 and the magnitude of experimental values of S_p , shows that the ratio of phonon to electron relaxation time, τ_p/τ_e , must be the order of $(10)^4$. When Herring substituted the result of his calculation for the phonon relaxation time, τ_p , into Equation 45, he obtained for an ideal semiconductor

$$S_p \propto T^{-7/2} \quad (46)$$

The following modifications should be considered if Equation 45 is to be compared to the data of an actual semiconductor:

- (a) The equation applies to most of the usual band structures, excluding the case of a degenerate band edge with spin-orbit splitting that is the order of kT .
- (b) The equation applies for slight or moderate amounts of impurity scattering or optical-mode scattering. Large amounts of impurity scattering would be expected to decrease the magnitude of the exponent 0.1 to 0.2.
- (c) The equation applies, strictly, only to a semiconductor in which longitudinal mode phonons predominate over transverse modes.
- (d) The equation applies when imperfection and boundary scattering are small. If these types of scattering aren't small, the temperature dependence will be smaller, possibly over the whole temperature range in which S_p is accurately measureable.
- (e) The equation applies to semiconductors with a small concentration of charge carriers; the effect of large carrier concentrations is discussed in Section III.

It was noted in Section IV. C. 2. that $|S_p|$ for the three purest Mg_2Si samples was very nearly proportional to T^{-3} over a fairly wide temperature range. This result seems to agree quite well with Herring's prediction, since, as was indicated in Section IV. D. 4., it is likely that impurity scattering was present at low temperatures. It is also possible that

boundary scattering was not negligible over the temperature range under consideration; this is confirmed by the fact that the sample size reduction for 34B-3, which is discussed in the next section, reduced the magnitude of S somewhat for all temperatures below 80°K (Figure 13). Some results for the temperature dependence of the phonon Seebeck coefficients in other semiconductors are shown in Table 7.

Table 7. Temperature dependence of S_p for other semiconductors

Semiconductor	Worker	Temperature dependence of $ S_p $
p-type germanium	Geballe and Hull (14)	-3.2
n-type germanium	Geballe and Hull (14)	-2.4
p-and n-type silicon	Geballe and Hull (15)	-2.3
diamond	Goldsmid, et al. (17)	-3.6
zinc oxide	Hutson (24)	-2.5

2. Boundary scattering

When the relaxation time of the phonons, effective in producing S_p , becomes comparable with the boundary scattering time (the thickness of the sample divided by the average sound velocity), the magnitude of S_p is expected to be smaller. This is the principal cause of the deviations at low temperatures of $|S_p|$ from the T^{-3} dependence in Figure 15. Thus when boundary scattering dominates, an upper limit for the magnitude of S_p may be obtained from Equation 45 with $\tau_p = L/\bar{c}$ and $\mu = e\tau_e/m$,

$$S_{PB} = \frac{L}{\mu T} \frac{1}{\bar{c}} \quad (47)$$

where L equals approximately 1.1 times the sample diameter for a square cross section and perfectly diffuse boundary scattering.

Application of Equation 47 to sample 34B-3 with: $\mu = 10^5$ cm/volt-sec; $T = 25^\circ\text{K}$; $L = 0.13$ cm; $\bar{c} = 7.5 \times 10^5$ cm/sec, Whitten (43); and $f = 1$, gives the result $S_{PB} \approx 30$ mv/deg. The fact that the measured $|S_p|$ in Figure 15 tends to bend over considerably below this boundary scattering limit is probably due partly to the saturation effect, discussed in the next section. Another possible cause of $|S_p| < |S_{PB}|$ is the fact that the quantity f in Equation 47 could be less than 1, that is a substantial part of the acoustical-mode scattering could be due to shear modes. The relaxation time for shear modes is much less than that for longitudinal modes, and consequently, $|S_p|$ is smaller for shear modes, Herring (19).

In the temperature range where boundary scattering predominates, S_p should be approximately proportional to the diameter of the specimen. An experimental verification of this size effect is provided by the results for sample 34B-3-I, having a thickness of 1.145 mm and 34B-3-II, which was the same sample with the thickness reduced to 0.867 mm. Figure 13 shows that in the temperature range 20°K to 40°K , the size reduction of 0.75 resulted in a reduction of the magnitude of S_p by about the same factor. Unfortunately, the measured Seebeck coefficients for 34B-3-II scattered considerably, preventing a more detailed quantitative check of the size effect. Geballe and Hull (14) and (15) have observed the size effect in both germanium and silicon.

The size effect probably also explains the reduction of $|S_p|$ of 31B-2 below that for 31B-3, Figure 15. Sample 31B-2 had a carrier concentration at 300°K of $5 \times 10^{16} \text{ cm}^{-3}$ compared to $7 \times 10^{16} \text{ cm}^{-3}$ for 31B-3, and thus, 31B-2 would be expected to have $|S_p|$ comparable to that of 31B-3. However, as mentioned in Section II. A. 3., the results of X-ray analysis showed that 31B-2 was divided along its entire length into two crystals differing in orientation by about 4 degrees, whereas 31B-3 proved to be a single crystal. Since the boundary (probably a twinning boundary) in 31B-2 does divide the sample into two roughly equal regions and if the twinning boundary has the same effect as the sample boundary in scattering phonons, it is likely that $|S_p|$ would be reduced to about 1/2. This is seen to be the case in Figure 15.

3. Saturation effect

Herring's theory (19), which predicted the temperature dependence for S_p of Equation 46, assumed a small carrier concentration, such that the perturbation of the phonon system by the charge carriers was small. According to Herring, an increase of the carrier concentration will decrease $|S_p|$, since increased phonon-electron scattering will reduce the thermal conduction energy flux and hence reduce the drag of the phonons on a given charge carrier. The prediction of Herring's detailed calculation is roughly the same as the effect of carrier concentration on S_p shown in Figure 15 (the carrier concentrations at 300°K were: $n = 2 \times 10^{18} \text{ cm}^{-3}$ for 28B-5 and $n = 3 \times 10^{16} \text{ cm}^{-3}$ for 34B-3).

B. Mobility Ratio and Effective Masses

1. Mobility ratio

Winkler (45) determined $b = 5.7$ for n-type Mg_2Si , using the same method described in Section IV. D. 3. His result is based on two samples for which he interpreted the temperature range 825°K to 1000°K as being intrinsic. He determined the slope of S versus $1/T$ from 4 points for one sample and from 3 points for the other. Since the result $b \approx 3.5$ for n-type Mg_2Si of this investigation is based on several samples exhibiting intrinsic behavior over temperature ranges as large as 350 degrees, the value $b \approx 3.5$ is thought to be more reliable than Winkler's value.

Morris, et al. (33), using Hall coefficient results, determined b for two p-type Mg_2Si samples. He used two methods both involving the Hall coefficient near $R = 0$ at about 500°K and obtained $b = 4.8$. Since the mobility ratio is, in general, temperature dependent, it is possible that $b = 4.8$ at 500°K and $b = 3.5$ in the range 700°K to 1000°K . Such a temperature dependence, however, is difficult to reconcile with the approximate temperature independence of b exhibited by n-type Seebeck coefficient data in the intrinsic range.

Because both Winkler's and Morris' values of b were substantially larger than 3.5, an additional determination of b was made using a method involving only resistivity data, Hunter (23). The data of Morris' p-type samples 26B-1 and 25B-2 as well as sample 40B-8 of this investigation were analyzed by this method. Unfortunately, the method is quite sensitive

to small uncertainties in the slope determination for n-type Mg_2Si because of the manner in which the resistivity approaches the intrinsic line. The results for the p-type samples are: for 26B-1, $b = 3.1$ for 25B-2, $b = 3.2$; for 40B-8, $b = 1.7$.

Howarth, et al. (21) observed a magnetic field dependence of the mobility ratio as determined by the method used by Morris. The work of this group on InSb showed variations in measured b of 100 per cent when H was varied. Unfortunately, time did not allow a check for possible field dependence of the Hall coefficient for p-type Mg_2Si near 500°K . Breckenridge, et al. (5) have also noted that for InSb, values of b from 29 to 85 have been reported.

Other possible explanations of the discrepancy between the different values of b are: a possible dependence of b on carrier concentration; or the fact that b for p-type Mg_2Si is simply different than b in n-type Mg_2Si . Both of these effects have been observed to produce differences in b of the order of 25 per cent for germanium, Prince (35).

Finally, it is possible that the pressure contact error in the Seebeck coefficient measurements, discussed in Section III. B. 5., increased with temperature during the course of the high temperature measurements. If the pressure contact error for sample 31B-3 had changed from an amount corresponding to $\alpha = 0.1$ at 300°K to an amount corresponding to 0.25 in the intrinsic temperature range, the resulting b would have been 5 instead of 3.5. The probability of this latter explanation is, however,

minimized by the fact that in the temperature range 300°K to 450°K, Seebeck coefficient measurements with both soldered contacts and pressure contacts for 34B-3 and 40B-8 indicated no systematic variation of α with temperature. Furthermore, in Section IV. D. 3. it was noted that α probably decreased rather than increased as the temperature increased.

2. Effective masses

Winkler (45) determined from Seebeck coefficient and Hall coefficient measurements, the effective masses $m_n = 0.36 m_0$ and $m_p = 0.72 m_0$. He determined $\beta = -6.4 \times 10^{-4}$ ev/deg from the intercept of Equation 41, using his value of $b = 5.7$, $E_{GO} = 0.76$ ev, $r_n = r_p = 2$ and $m_n/m_p = b^{-2/5}$. The latter relationship is true for longitudinal acoustical-mode scattering if the holes and electrons have equal deformation potentials, Shockley (39, page 278). Winkler then determined $m_n m_p$ from Hall data by a method similar to that used to obtain Equation 40. As Winkler points out in his paper, his mass determinations are only approximate because of the assumptions made.

Morris (32) using Winkler's β , $b = 4.8$, and $E_{GO} = 0.79$ ev in the intercept of Equation 39 for his Hall data, also determined the effective masses. His results, $m_n = 0.46 m_0$ and $m_p = 0.87 m_0$, agree reasonably well with Winkler's. This agreement is expected, since both sets of results were based on the same value of β and nearly the same E_{GO} ; the calculation is most sensitive to E_{GO} and β , since $m_n m_p$ depends exponentially on these quantities.

The above mass determinations of Winkler and Morris are consistent

with acoustical mode scattering, since $r = 2$ (see Table 5) and $m_n/m_p = b^{-2/5}$ were used in the calculations. The results of the intrinsic Hall and Seebeck as well as extrinsic Seebeck data of this investigation, implying $m_n = 0.44 m_0$ and $m_p = 2.2 m_0$, were shown in Section IV. D. 5. to be more consistent with optical-mode scattering, whose importance is suggested by the observed Hall mobility (Morris, et al. (33)).

C. Conclusions

The low temperature Seebeck coefficient of Mg_2Si has been interpreted in terms of a phonon drag effect. The Seebeck coefficient at low temperatures consisted of two terms: the ordinary term, S_e , resulting from the diffusion of charge carriers from hot to cold; and a phonon contribution, S_p , resulting from a dragging of the charge carriers by phonons. The phonon Seebeck coefficient exhibited behavior which agreed qualitatively, and quantitatively to the extent that it could be checked, with the theory of Herring (19). $|S_p|$ was proportional to T^{-3} for the purest n-type samples above the boundary scattering temperature range.

For temperatures higher than 200°K, the phonon Seebeck coefficient was small and the measured Seebeck coefficients for both p-type and n-type Mg_2Si agreed with the predictions of the usual theory for a non-degenerate semiconductor.

The ratio of electron to hole mobility was found to be essentially constant for the purer n-type samples in the intrinsic temperature range (600°K to 1000°K) and to have the value, $b \approx 3.5$. The value $b \approx 3.5$ is

somewhat lower than the value $b \approx 5$ found by Morris, et al. (33) from Hall data on p-type samples at about 500°K; however, Morris' resistivity data on his p-type samples implied $b \approx 3.2$ for $T \approx 500^\circ\text{K}$. ✓

The effective masses determined from extrinsic Seebeck coefficient data were found to be in agreement with the effective masses estimated from intrinsic Hall and Seebeck data, if optical-mode scattering predominated in the purer n-type samples and ionized impurity scattering was comparable with optical-mode scattering for the impure p-type samples at 300°K. The effective masses were found to be $m_n \approx 0.4 m_0$ and $m_p \approx 2 m_0$. ✓

D. Future Work

More complete Seebeck coefficient data for samples with a range of carrier concentration and a range of sample size would enable a more detailed quantitative comparison of phonon drag Seebeck theory and experiment. Thermal conductivity measurements of Mg_2Si at low temperatures would provide some useful information about phonon relaxation times to compare with phonon drag results. A study of the Seebeck effect in the other members of the Mg_2X family of compounds would also prove interesting.

Other possible areas of investigation closely related to the Seebeck effect are: the magneto-Seebeck effect, which can yield similar information to that obtainable from the analogous magneto-resistance effect; and the Nernst effect, which, like the Seebeck effect, has a phonon drag contribution. These studies would require oriented specimens with a high.

degree of uniformity.

As was pointed out in Section IV. D. 5., if the effective mass and band structure were known from cyclotron resonance, magneto-resistance, and other measurements, deductions could be made concerning the scattering mechanisms. On the other hand, if the scattering mechanisms could be definitely established with the aid of knowledge of such quantities as the dielectric constant, and the Debye temperature, information concerning the effective masses could be obtained from the Seebeck effect measurements. Further study of the optical properties could give a more precise determination of β as well as information about the band structure.

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VII. APPENDIX

Table 8. Experimental results, sample 28B-5

Temperature T deg K	Seebeck Coefficient -S microvolts/deg	Hall Coefficient -R cm ³ /coulomb	Resistivity ρ ohm-cm
7.5	108.0	3.11	5.68×10^{-3}
10.0	123.8	4.40	5.86
13.0	-	4.40	6.07
14.6	182.3	-	-
18.0	-	4.38	6.35
19.0	188.2	-	-
27.0	268.9	4.43	6.70
31.1	304.7	4.50	6.85
36.2	348.2	-	-
45.0	375.3	4.85	6.98
51.3	416.7	5.05	6.94
60.0	373.7	5.22	6.85
68.0	367.3	5.34	6.73
76.4	364.9	5.40	6.61
84.2	359.5	5.43	6.53
90.0	353.9	5.38	6.45
103.3	346.5	5.28	6.43
112.5	342.7	5.24	6.46
126.5	341.8	5.12	6.60
136.8	339.8	5.05	6.74
153.8	345.0	4.97	7.10
170.7	345.2	4.88	7.55
190.7	350.7	4.80	8.16
210.7	355.3	4.72	8.54
231.3	365.5	4.65	9.74
255.5	371.4	4.61	10.83
284.4	375.2	4.56	12.32
299.3	394.3	4.56	13.15
298.3	334.9	4.54	13.14
340	338.4	4.64	15.58

Table 8. (Continued)

Temperature T deg K	Seebeck Coefficient -S microvolts/deg	Hall Coefficient -R cm ³ /coulomb	Resistivity ρ ohm-cm
390	383.3	4.50	18.93 x 10 ⁻³
455	395.4	4.57	23.72
514	422.5	4.73	28.65
590	402.0	3.83	33.37
665	318.0	2.47	30.02
735	239.9	1.22	22.00
810	184.2	0.63	15.06
882	152.5	0.33	10.55
956	126.9	0.19	7.58

Table 9. Experimental results, sample 31B-2

Temperature T deg K	Seebeck Coefficient -S microvolts/deg	Hall Coefficient -R cm ³ /coulomb	Resistivity ρ ohm-cm
8.0	639.0	-	-
10.0	-	417.5	3118.5 x 10 ⁻²
11.7	789.4	-	-
12.0	-	30779	734.9
16.4	862.5	5676	150.12
19.2	946.3	2993	80.42
26.0	1082.4	1344	33.98
34.2	1212.2	770.1	17.65
45.0	1103.5	514.9	10.32
56.5	909.0	369.6	6.92
65.8	788.6	310.3	5.67
74.7	730.1	283.6	-
78.7	696.2	275.0	5.04
89.0	676.4	259.5	4.89
100.6	643.6	247.0	5.24
112.5	631.1	233.7	5.89
126.1	612.9	221.6	6.91
139.6	603.2	209.9	8.09
154.4	597.1	199.2	9.66
167.6	596.8	191.4	11.24
184.2	610.1	182.9	13.19
199.3	602.8	177.8	15.29
213.5	612.7	174.7	17.76
233.6	624.7	170.5	21.05
255.1	637.2	166.9	25.09
269.9	652.9	-	-
276.7	-	164.0	29.27
283.8	656.2	162.6	30.85
295.7	664.8	161.8	33.30
300.6	666.4	160.7	34.39
313.2	674.0	159.6	37.10
333.5	577.7	166.0	41.15
365.4	587.5	160.3	48.16
392.5	585.0	150.9	53.17

Table 9. (Continued)

Temperature T deg K	Seebeck Coefficient -S microvolts/deg	Hall Coefficient -R cm ³ /coulomb	Resistivity ρ ohm-cm
420.4	583.1	124.8	53.61 x 10 ⁻²
453.0	466.9	86.38	45.29
488.5	375.5	47.02	31.74
518.1	345.5	28.08	22.43
547.1	279.2	16.91	15.88
579.6	249.6	9.890	10.97
617.7	221.6	5.519	7.195
657.9	201.0	3.354	4.857
692.2	185.7	1.886	3.613
727.5	179.3	1.485	2.726
774.2	163.3	0.924	1.968
820.2	154.5	0.577	1.470
868.8	141.4	0.356	1.127
918.9	128.3	0.235	0.883
967.1	117.5	0.177	0.778

Table 10. Experimental results, sample 31B-3

Temperature T deg K	Seebeck Coefficient -S microvolts/deg	Hall Coefficient -R cm ³ /coulomb	Resistivity ρ ohm-cm
6.0	-	-	5626 x 10 ⁻²
6.9	1264.0	-	-
9.0	1747.2	85423	2841
14.5	2024.3	6718.2	151.4
18.5	-	2509.0	51.24
19.0	2071.5	-	-
25.5	2070.1	1001.2	19.23
30.0	2028.3	732.9	13.31
36.5	1836.2	527.5	9.09
40.1	1667.6	455.2	7.64
44.7	1524.0	380.9	6.37
51.0	1217.6	310.2	5.25
61.0	938.8	253.5	4.27
65.3	888.8	232.4	4.02
75.0	724.8	203.1	3.75
80.0	718.4	192.1	3.71
86.0	689.9	182.3	3.74
95.4	659.8	170.2	3.92
106.1	622.5	160.4	4.16
120.2	601.4	149.9	4.96
136.0	594.2	140.3	5.93
150.2	581.7	132.6	6.96
170.0	578.5	124.7	8.58
194.8	585.5	117.6	10.60
217.8	586.1	112.5	12.93
244.5	613.3	108.3	15.93
269.3	604.0	-	-
293.0	543.9	106.9	22.69
299.5	-	102.4	23.08
327.0	568.3	104.3	27.61
354.5	585.8	100.4	31.71
383.5	594.8	100.0	36.05
415.1	598.5	91.84	39.61
449.8	543.0	73.80	38.45
482.7	460.3	48.18	31.31

Table 10. (Continued)

Temperature T deg K	Seebeck Coefficient -S microvolts/deg	Hall Coefficient -R cm ³ /coulomb	Resistivity ρ ohm-cm
513.8	383.5	27.61	22.97x10 ⁻²
548.0	312.0	16.22	15.65
587.4	264.6	8.719	10.08
622.5	232.2	5.189	7.005
664.3	209.7	3.025	4.718
704.0	192.6	1.887	3.358
746.9	177.3	1.189	2.411
793.7	162.5	0.6968	1.778
842.9	146.7	0.3862	1.330
897.1	134.4	0.2875	0.996
943.6	121.5	0.2278	0.799
989.0	111.1	0.0521	0.677

Table 11. Experimental results, sample 34B-3-I

Temperature T deg K	Seebeck Coefficient -S microvolts/deg	Hall Coefficient -R cm ³ /coulomb	Resistivity ρ ohm-cm
5.0	140.3	-213.5	8200.7 x 10 ⁻²
8.5	311.1	40902	7649.4
12.0	1980.6	145288	-
12.8	-	-	1813.9
16.4	2892.9	29218	340.2
21.5	3200.4	7957	87.87
29.8	2699.2	3359	31.72
37.5	2114.2	1955	17.74
44.1	1697.3	1287	11.30
49.9	1445.1	982.8	8.641
58.7	1119.6	750.4	6.834
64.4	996.8	661.1	6.321
72.5	888.7	582.1	5.999
79.8	807.8	530.5	6.053
88.3	756.8	491.6	6.396
90.2	748.1	484.0	6.516
101.7	712.1	444.6	7.440
115.2	680.2	407.5	8.941
130.3	660.3	372.3	10.99
143.3	655.9	349.3	13.11
158.5	648.3	328.7	15.94
175.5	645.6	312.6	19.51
195.2	652.9	299.8	24.28
223.5	-	287.1	32.22
249.9	662.1	279.9	40.46
280.0	686.0	272.4	50.90
299.2	694.4	268.4	58.03

Table 12. Experimental results, sample 34B-3-II

Temperature T deg K	Seebeck Coefficient $\frac{\Delta S}{\Delta T}$ microvolts/deg	Hall Coefficient -R cm ³ /coulomb	Resistivity ρ ohm-cm
6.1	-	506.4	6447.1 x 10 ⁻²
7.5	131.0	-	-
9.1	377.2	80614	5767.7
11.4	1391.6	193441	3341.1
14.3	2058.8	58209	715.16
18.1	2233.3	-	-
18.6	-	15573	178.24
22.1	2465.7	7508	86.24
26.2	2190.2	-	-
29.8	2165.4	3317	32.26
34.4	2065.1	-	-
39.5	1726.4	1651	14.71
45.1	1512.5	-	-
52.2	1245.1	904.3	8.054
58.6	1025.6	-	-
66.0	880.1	632.0	6.180
74.4	820.2	-	-
81.8	797.3	517.9	6.117
90.0	744.5	481.8	6.525
115.4	663.3	404.5	8.957
150.5	632.2	336.6	14.41
194.4	633.1	297.9	24.23
248.2	653.7	279.5	40.14
299.8	678.5	267.8	58.66
331.5	475.9	269.9	74.64
360.2	491.0	257.2	85.06
386.8	495.2	229.5	90.02
421.4	450.0	160.8	85.84
455.5	368.3	92.14	54.34
487.5	305.9	48.14	35.47

Table 12. (Continued)

Temperature T deg K	Seebeck Coefficient $-S$ microvolts/deg	Hall Coefficient $-R$ $\text{cm}^3/\text{coulomb}$	Resistivity ρ ohm-cm
524.1	251.8	25.07	21.77×10^{-2}
558.5	217.5	13.85	14.11
585.3	219.8	9.06	10.14
618.4	201.0	5.62	7.156
652.3	190.1	3.53	5.124
693.1	175.1	2.17	3.570
735.9	164.6	1.25	2.551
773.9	158.1	0.853	1.944
818.6	146.5	0.550	1.468
863.8	137.9	0.360	1.230
913.5	123.4	0.133	0.866
973.5	110.8	0.051	0.673

Table 13. Experimental results, Sample 40B-4

Temperature T deg K	Seebeck Coefficient $\bar{S}$ microvolts/deg	Hall Coefficient $\bar{R}$ cm ³ /coulomb	Resistivity ρ ohm-cm
7.8	25.4		
10.0	-		
13.3	122.6		
17.0	194.2		
21.0	276.7		
25.4	373.8		
29.8	441.5		
37.7	-		
38.7	663.9		
43.3	742.3	19.470	
50.0	784.6	15.338	
58.9	826.3	12.707	
69.7	769.1	11.486	
80.5	723.1	8.257	
94.7	679.1	-	
100.3	-	6.453	7.815×10^{-2}
119.9	598.3	-	-
125.6	-	5.990	5.655
150.5	550.9	4.762	4.080
175.1	538.6	4.329	3.530
200.7	533.9	4.008	3.740
224.7	521.8	3.747	4.060
244.1	533.5	-	-
249.3	-	3.575	4.443
269.1	537.7	3.464	4.748
299.1	551.8	3.260	5.288

Table 14. Experimental results, sample 40B-8

Temperature T deg K	Seebeck Coefficient S microvolts/deg	Hall Coefficient R cm ³ /coulomb	Resistivity ρ ohm-cm
10.0	34.4		
13.3	94.8		
16.6	177.0		
21.4	328.2		
25.1	393.1		
30.5	570.8		
38.0	711.7		
45.0	797.7		
52.4	873.5		
62.2	777.3		
69.4	755.1		
78.9	738.5		
79.6	-	7.860	7.496×10^{-2}
85.8	689.9	-	-
87.3	-	7.399	6.696
94.9	635.2	-	-
96.4	-	6.264	5.987
106.2	595.4	6.001	5.310
116.0	578.2	5.340	4.675
125.5	561.9	5.299	4.155
151.0	553.2	4.432	3.727
170.5	532.7	-	-
181.0	-	4.199	3.475
194.5	554.8	-	-
215.1	546.4	3.794	3.869
231.5	554.5	-	-
249.7	562.8	3.566	4.391
274.5	572.0	3.453	4.821
297.4	581.4	3.394	5.248
300.0	563.1	3.418	5.312

Table 14. (Continued)

Temperature T deg K	Seebeck Coefficient S microvolts/deg	Hall Coefficient R cm ³ /coulomb	Resistivity ρ ohm-cm
302.0	399.2	2.860	5.380×10^{-2}
340.1	413.7	3.085	6.114
376.6	437.1	3.091	6.841
409.4	460.2	2.992	7.715
443.0	469.0	3.235	8.236
472.7	-	2.405	9.123
480.1	436.7	-	-
523.0	400.3	1.987	9.774
561.6	308.5	0.447	9.695
598.4	207.3	-0.626	8.621
639.7	88.6	-1.623	6.633
680.7	-4.3	-1.495	4.720
725.6	-70.3	-1.163	3.285
768.7	-101.0	-0.8581	2.318
819.2	-111.4	-0.4673	1.660
870.4	-114.6	-0.3142	1.191
916.4	-110.4	-	0.907
966.8	-105.7	-0.1601	0.7421

Table 15. Absolute Seebeck coefficient of gold-cobalt and copper

Temperature (°K)	$S_{\text{Au-Co}}$ ($\mu\text{V}/\text{deg}$)	S_{Cu} ($\mu\text{V}/\text{deg}$)	Temperature (°K)	$S_{\text{Au-Co}}$ ($\mu\text{V}/\text{deg}$)	S_{Cu} ($\mu\text{V}/\text{deg}$)
15	-12.3	0.20	115	-36.5	1.15
20	-15.8	0.42	120	-36.8	1.14
25	-18.4	0.64	125	-36.9	1.13
30	-20.2	0.81	130	-36.9	1.13
35	-22.1	0.95	135	-37.2	1.13
40	-24.2	1.06	140	-37.9	1.13
45	-25.9	1.14	145	-38.3	1.14
50	-27.2	1.21	150	-38.7	1.14
55	-28.5	1.27	155	-38.1	1.15
60	-29.8	1.31	165	-38.3	1.18
65	-31.0	1.34	175	-38.6	1.21
70	-31.6	1.36	185	-38.7	1.26
75	-32.4	1.37	195	-38.7	1.31
80	-33.3	1.35	205	-38.8	1.36
85	-33.7	1.33	215	-38.8	1.41
90	-34.3	1.30	225	-38.8	1.47
95	-35.0	1.26	235	-38.8	1.52
100	-35.6	1.22			
105	-35.8	1.19			
110	-36.0	1.16			

Table 16. Absolute Seebeck coefficient of constantan and chromel

Temperature (°C)	S _{Constantan} (μ v/deg)	S _{Chromel} (μ v/deg)	✓
0	-36.8	21.20	
20	-38.5	21.55	
50	-41.0	22.05	
100	-44.6	22.90	
150	-47.6	23.72	
200	-50.4	24.07	
250	-52.8	23.70	
300	-54.9	23.17	
350	-56.7	22.78	
400	-58.4	22.15	
450	-59.8	21.53	
500	-61.0	20.76	
550	-62.1	19.67	
600	-63.1	18.57	
650	-63.8	17.42	
700	-64.5	16.24	