has been found in many liquid alloys which belong to the compound systems of Sauerwald.[20]

In conclusion, one may say that the assumption of chains in the liquid and a gradual change of predominantly metallic bonding at very high temperatures makes it possible to understand the semiconducting properties of liquid tellurium and the gradual transition to metallic conduction at high temperatures.[21,22]

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[20] F. Sauerwald, Z. Metallkunde **35**, 105 (1943); **41**, 97 (1950); **41**, 214 (1950).

[21] After this work was completed we learned that there are a number of Russian papers[22] which discuss liquid semiconductors. However, these papers do not contain any Hall effect measurements and are not carried out with material of the purity which we have been able to produce.

[22] Blum, Mokrovskii, and Regel, Izvest. Akad. Nauk **16**, 139 (1952); N. P. Mokorovskii and A. P. Regel, J. Tech. Phys. (U.S.S.R.) **25**, 2093 (1955).

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Electrical Properties of Boron Single Crystals*

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The electrical resistivity, Hall coefficient, and thermoelectric power of microscopic boron single crystals have been measured as a function of temperature. Rectification and photoconductivity effects were observed at room temperature. The large majority of these single crystals had a high resistivity (about 1.7×10^6 ohm cm at 300°K) which decreased by a factor of nearly 10^{10} as the temperature was increased from 200°K to 1000°K. A few crystals, however, had a much lower resistivity at 300°K (less than 100 ohm cm) and at this temperature their resistivity decreased much more slowly with increasing temperature. Such behavior is attributed to donor impurity levels. From data in the high-temperature range (800°K to 1000°K) the energy gap between the filled band and conduction band was calculated to be 1.55 ± 0.05 ev. Hall, thermoelectric, and rectification studies indicated that hole conduction predominated for all crystals at high temperatures but that electron conduction predominated for the low-resistivity crystals near 300°K. The mobilities of the charge carriers at 300°K were found to be the order of one cm^2 volt^{-1} sec^{-1} with the hole mobility the larger. Non-ohmic conduction was observed and shown to arise from Joule heating.

I. INTRODUCTION

Of the semiconducting elements, boron is perhaps the least understood with regard to the electrical properties of single crystals. Theoretical calculations of the electronic structure are difficult, owing to the extremely complicated crystal structure. Hoard, Geller, and Hughes[1] find 50 atoms in a tetragonal unit cell having $a_0=8.73\pm0.02$ A and $c_0=5.03\pm0.02$ A. Forty-eight atoms are at the vertices of four nearly regular icosahedra which are centered tetrahedrally and linked so that each boron atom has six bonds to the corners of a pentagonal pyramid. The mean distance to the six neighbors is between 1.75 and 1.80 A. The remaining two atoms form only tetrahedrally directed bonds to complete the network. Experimentally, adequate resistivity and Hall measurements on single crystals have not been reported because of the lack of large specimens.

The electrical resistivity of polycrystalline boron was first measured by Weintraub[2] and later by Warth,[3] Freymann and Stieber,[4] and others; a summary has been written by Moss.[5] More recently, the thermoelectric power and other electrical properties of polycrystalline samples have been reported by Lagrenaudie,[6] by Uno, Irie, Yoshida, and Shinohara,[7] and by Jacobsmeyer, Friedrich, and Badar.[8] These investigations show that boron is a semiconductor with hole conductivity predominant at high temperatures.

The present investigation[9,10] is the first in which single crystals have been studied. This work was made possible by the development of micromanipulative techniques previously reported.[11]

The single crystals were grown by Huibregtse and

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* This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

† Present address: Naval Ordnance Test Station, China Lake, California.

[1] Hoard, Geller, and Hughes, J. Am. Chem. Soc. **73**, 1892 (1951).

[2] E. Weintraub, Trans. Am. Electrochem. Soc. **16**, 165 (1909); J. Ind. Eng. Chem. **5**, 106 (1913).

[3] A. H. Warth, Trans. Am. Electrochem. Soc. **47**, 62 (1925).

[4] R. Freymann and A. Stieber, Compt. rend. **199**, 1109 (1934).

[5] T. S. Moss, *Photoconductivity in the Elements* (Academic Press, Inc., New York, 1952), Chap. II, especially pp. 89–92.

[6] J. Lagrenaudie, J. phys. radium **13**, 554 (1952); **14**, 14 (1953).

[7] Uno, Irie, Yoshida, and Shinohara, J. Sci. Research Inst. Tokyo **47**, 216 and 223 (1953). A typographical error seems to exist in Fig. 3, p. 218. The activation energy 0.44 ev should probably read 1.44 ev.

[8] Jacobsmeyer, Friedrich, and Badar, Office of Ordnance Research Project No. 627, Final Report, St. Louis University, October 15, 1954 (unpublished); Phys. Rev. **91**, 492 (1953); **94**, 808 (1954).

[9] Preliminary results have been presented at American Physical Society meetings: Shaw, Hudson, and Danielson, Phys. Rev. **89**, 900(A) (1953); **91**, 208(A) (1953).

[10] Shaw, Hudson, and Danielson, U. S. Atomic Energy Commission Report ISC-380, August, 1953 (unpublished).

[11] Shaw, Hudson, and Danielson, Rev. Sci. Instr. **26**, 237 (1955); W. C. Shaw, Rev. Sci. Instr. **26**, 238 (1955).

Shinn[12] by the reduction of boron tribromide with hydrogen upon contact with a hot tantalum filament. The method has been described by Laubengayer, Hurd, Newkirk, and Hoard.[13] The largest crystals (weighing about 5 micrograms) were about 0.1 mm by 0.1 mm by 0.3 mm.

The crystals were examined by optical, x-ray, and spectroscopic methods. Microscopic examination showed that faces characteristic of a tetragonal single crystal were clearly visible. Laue patterns showed the specimens to be single crystals but in some cases doubling of spots suggested twinning. Spectroscopic analyses of the original agglomerates showed no detectable metallic impurities except tantalum and silver; both of these were completely removed by chemical cleaning. Impurity concentrations too small to be detected spectroscopically could, however, greatly affect the electrical properties.

II. RESISTIVITY MEASUREMENTS

A. Apparatus and Procedure

Photomicrographs of microscopic boron crystals mounted for conductivity measurements are shown in Figs. 1 and 3 of reference 11. The method of mounting has been described elsewhere.[10,11]

Figure 1 shows a block diagram of the universal potentiometer which was used to measure probe potentials and crystal current. In use, the potential of a probe (*P*) was matched to that of the slider on the helipot (*H*) by means of the impedance-transforming vacuum tube electrometer (*E*) and the galvanometer (*G*). The crystal resistance was found by comparison with the precision series element (*S*), using ratios obtained with the precision potential divider (*D* and *H*).

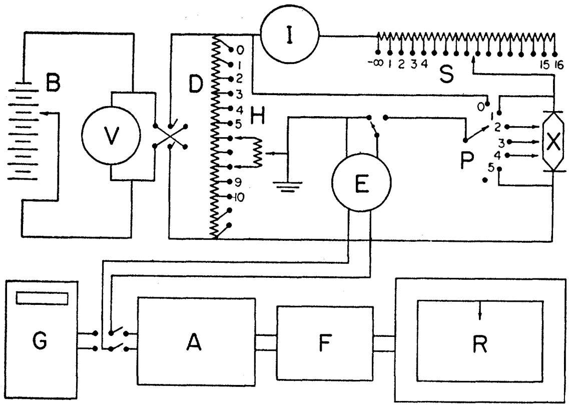

FIG. 1. Circuit for resistivity and Hall measurements. *B*: battery, to 180 v; *V*: Voltmeter (vacuum tube); *D*: potential divider, 120 K by 20 K; *H*: helipot, 100 K; *I*: microammeter; *S*: series resistance, 100 megohm by powers of $\sqrt{10}$; *E*: electrometer (vacuum tube); *P*: probe selector; *X*: crystal; *G*: galvanometer; *A*: amplifier, dc; *F*: filter; *R*: recorder.

Measurements above room temperature were carried out with the crystal mount in a constant temperature furnace. Measurements at temperatures between 25°C and −80°C were carried out with the crystal mount contained in a desiccated test tube immersed in coolant. At low temperatures the resistance was too high for the circuit of Fig. 1. In this case, an electrometer was used to measure the crystal current.

The procedure employed with crystal No. 46 (Fig. 1 of reference 11) is illustrative of the measurements. Preliminary experience on discarded crystals indicated the regions of temperature and current which were safe to use without electrical or physical damage to the sample. The potentials of all probes were obtained as a function of crystal current with the furnace at room temperature (25°C); these data were entirely reproducible. At higher temperatures data were confined to the ohmic region of resistance. Data were first taken from 25°C to 150°C and back to 25°C. Low-temperature measurements were then made between 25°C and −80°C. The crystal was encased in ceramic cement (Sauereisen No. 29) and returned to the furnace for measurements between 25°C and 750°C. Below +80°C the finite resistance of the mounting was significant but at 150°C the previous data were reproduced. Variations on this procedure were carried out with numerous crystals. Some were successfully carried to 450°C and one to 650°C in uncemented mounts. In most cases the high-temperature data were obtained with the end probes alone. It was shown that the effects of contact resistance were negligible at all temperatures and that the data gave an accurate indication of the temperature dependence of resistivity.

An interesting feature of the electrical properties of the tiny crystals is their apparently non-ohmic conductivity over a wide temperature range. The effect was shown to arise from Joule heating. Whenever necessary, resistance values were reduced to those appropriate to zero current.[10]

B. Results

Resistance data were taken on twenty-eight crystals. Twenty-three had substantially identical characteristics; this behavior will be called "typical" for our crystals. Three had somewhat lower resistivity and two departed radically from typical behavior. The two anomalous specimens (Nos. 103, 104) were especially selected for low resistivity in exploratory tests on over 250 crystals. Many of the tiny crystals had irregular shapes but four were selected for the determination of resistivity from dimensional data. The resistivities of the others were determined by normalization at high temperatures.

Table I shows the room temperature resistivities of eight boron crystals. The room-temperature resistivity

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[12] A. G. Shinn, M.S. thesis, Iowa State College Library, Ames, Iowa, 1950 (unpublished).

[13] Laubengayer, Hurd, Newkirk, and Hoard, J. Am. Chem. Soc. **65**, 1924 (1943).

TABLE I. Resistivity of boron at 300°K.

Crystal number	46	30	40	47	45	23(*b*)	103	104
Width (microns)		91	80			110		140
Thickness (t) (microns)		74	87			94		130
Diameter (microns)	126			114	110			
Segment length (L) (microns)	112	121		171	83			
Total length (microns)	270	145	150	410	270	170		320
Segment resistance (R) (megohms)	150	300		200	45			
Total resistance (megohms)	480	3100	1100	1300	240	0.55	0.019	0.14
Resistivity (ρ) (megohm cm) from dimensions	1.7	1.7		1.2	0.52			
Resistivity (megohm cm) from normalization	1.7[a]	1.7	1.7	1.3	0.50	2.7×10^{-3}	4.9×10^{-5}	6.1×10^{-4}
Energy gap (E_g) (ev)	1.6	1.6		1.6	1.5	1.4	1.7	1.6

[a] By definition this resistivity is 1.7 megohm cm (see text).

(ρ) of each of the four crystals 46, 30, 47, and 45 was calculated directly from the equation $\rho = RA/L$, where R is the segment resistance reduced to zero current. The segment length (L) and other dimensions for computing the cross-sectional area (A) were measured with the aid of a calibrated microscope reticule. Crystals 30, 40, 23, and 104 were approximately rectangular in cross section while crystals 45, 46, and 47 were approximately circular. Instrumental errors in resistance measurements were less than 1%. The uncertainty in absolute resistivity arising from dimensional uncertainties was approximately 15% (standard deviation).

The resistivity of the typical crystal 46 was determined over the temperature range 200°K to 1000°K. The resistivity of the other crystals was then obtained by normalization of total (end to end) resistance data at high temperatures (800°K to 1000°K). Over this temperature range, all crystals were assumed to have the same resistivity and the same dependence of resistivity upon absolute temperature as would be expected in the intrinsic range. The resistivity at 300°K obtained by normalization at 900°K and the resistivity at 300°K obtained from the measured dimensions can be compared in Table I for crystals 30, 47, and 45. The agreement is better than would be expected from the dimensional uncertainty and affords considerable justification for this reasonable normalization procedure. Crystals 30 and 40, like crystal 46, were typical crystals with a resistivity of 1.7 megohm cm at 300°K. Crystals 47, 45, 103, and 104 had lower resistivities owing, undoubtedly, to higher impurity concentrations.

The variation of the logarithm of resistivities with the reciprocal of the absolute temperature is shown in Fig. 2. The resistance as a function of temperature for each of twenty-eight boron crystals was measured in the temperature range 300°K to 600°K. In the case of thirteen of these crystals the temperature range was extended to 1000°K. The typical behavior is exemplified by crystal 46; in the temperature range from 200°K to 1000°K its resistivity decreased by ten orders of magnitude. All crystals showed a decrease in slope of $\log_{10}\rho$ with increasing values of $1/T$, although the change in slope became very small at high temperatures where boron appeared to behave as a simple intrinsic semiconductor. In comparison with the typical behavior, crystals 45 and 18 had a somewhat lower resistivity at low temperatures. Crystals 103 and 104 had a much lower resistivity at low temperatures; such crystals, which must have a much higher concentration of donors or acceptors, were rare. Crystals 22 and 23 were particularly interesting since originally both were typical crystals similar to crystal 46. After these crystals were heated, either by means of a high furnace temperature or by means of a large current, permanent changes in the resistivity were produced as shown in the curves 22(*b*), 22(*c*), and 23(*b*). The observed effect suggests that heat treatment of a boron crystal may introduce imperfections capable of contributing charge carriers.

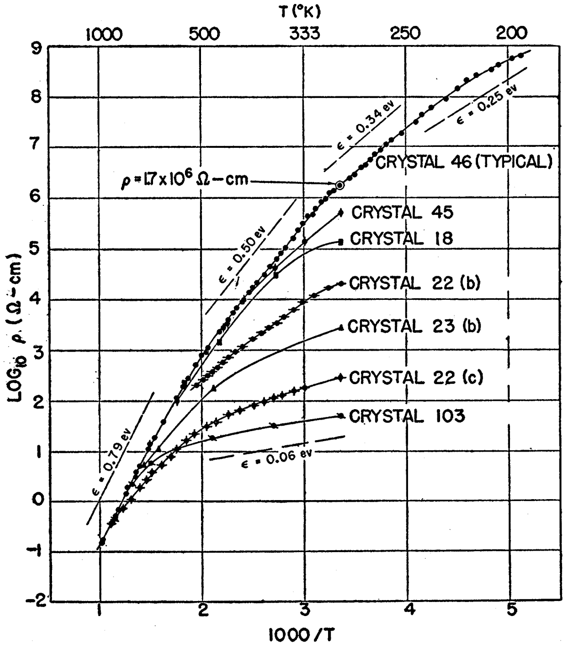

FIG. 2. Resistivity of boron single crystals. Values for ϵ obtained from $\rho \sim \exp(\epsilon/kT)$.

TABLE II. Hall effect data for boron.

Crystal number and material	Run No.	H_z Magnetic field (gauss)	V_x Crystal voltage (volts)	I_x Crystal current (μa)	ρ Normalized resistivity (ohm cm)	Crystal temperature (°C)	V_y Hall voltage (μv)	R_H Hall coefficient (cm³/coul)
26, antimony	1	7500	0.48	300 000	41.7×10^{-6}	25	$+80\pm5$	$+0.028\pm0.002$
50, germanium	2	8600	9.4	6850	2.2	25	−48 600	-6600 ± 700
	3	6900	9.4	6870	2.2	25	−45 300	
	4	5200	9.4	6890	2.2	25	−30 200	
	5	2600	9.4	6900	2.2	25	−18 500	
	6	1500	9.4	6910	2.2	25	− 8400	
104, boron	7	7000	31.2	375	360	62	-220 ± 40	-110 ± 23
	8	7000	52.7	740	310	75	-160 ± 80	-40 ± 20
	9	18 000	52.7	740	310	75	-310 ± 100	-30 ± 10
	10	18 000	12.0	104	500	34	-210 ± 60	-146 ± 42
	11	18 000	−12.0	−103	500	34	$+210\pm70$	-147 ± 49
	12	18 000	12.2	107	490	36	-180 ± 50	-126 ± 37
	13	14 400	12.2	107	490	36	-150 ± 50	-130 ± 45
	14	11 200	12.2	107	490	36	-120 ± 40	-134 ± 47
	15	5800	12.2	107	490	36	-70 ± 35	-150 ± 75
	16	18 000	2.68	18.7	610	24	-100 ± 20	-400 ± 120
	17	18 000	12.0	106	480	38	-170 ± 30	-120 ± 25
	18	18 000	31.5	342	390	53	-410 ± 100	-90 ± 25
	19	18 000	44.8	598	320	71	-410 ± 190	-50 ± 30
	20	18 000	76.2	1250	260	93	-150 ± 40	-9 ± 3
	21	18 000	93.0	1800	220	106	-84 ± 67	-4 ± 3
	22	18 000	99.0	3570	120	180	$+140\pm80$	$+3\pm2$
	23	18 000	103	5500	80	229	$+30\pm15$	$+0.4\pm0.3$
23(*b*), boron	24	10 000	48.4	89	2500	28	-250 ± 100	-2650 ± 1100
40, boron	25	18 000	39.6	0.0378	1.7×10^{6}	25	$+220\pm180$	$+(2.8\pm2.3)\times10^{5}$

III. HALL-EFFECT MEASUREMENTS

A. Apparatus and Procedure

No Hall measurements on single crystals of boron have been published, and only one preliminary study of polycrystalline samples has been reported.[8] The present work is a preliminary investigation to determine the orders of magnitude involved. Measurements on the tiny crystals were impeded by difficulties in mounting.[11] However, the most serious limitation was the electrical noise characteristic of small, high-resistance semiconductors.[14] For our minute crystals the noise was comparable to the Hall voltage, and a statistical procedure was required. Practical problems involved in the mounting of extra probes resulted in the selection of the single-probe method.[15] In the Appendix it is shown that the Ettingshausen effect was negligible.

The Hall effect was studied with the apparatus already described (Sec. IIA, Fig. 1). In this case balance was indicated by the Keithley Model 29 electrometer (*E*) followed by a Liston-Folb Model 10 amplifier (*A*). The filter (*F*) removed the high-frequency components from the electrical noise so that the unbalance signal could be satisfactorily recorded by the Brown strip-chart recorder (*R*). Noise was the only significant source of error in the Hall voltage. Auxiliary experiments showed that the noise originated almost entirely within the crystal. Before extensive data were taken on boron, double probe and single probe measurements were made on microscopic specimens of antimony and *n*-type germanium as part of the program for checking out the apparatus and method of mounting. Noise was not a problem, and a normal field and current reversal procedure was adequate. Satisfactory agreement between the single and double probe results was obtained. The values for the Hall coefficients of both materials were also very reasonable (see Table II).

A typical measurement on boron proceeded somewhat as follows: Equilibrium was established with crystal current flowing and the field off under conditions of best average potentiometer balance. The chart was (repeatedly) calibrated in terms of unbalance signal by a standard known alteration of the helipot. The recorder trace exhibited slow fluctuations characteristic of the low-frequency components of the crystal noise. The magnetic field was then applied for 40 seconds in each direction. The Hall effect could sometimes be seen superimposed upon the noise but individual Hall deflections were pronounced only during quiet intervals. As many as 400 reversals were taken in a given run, and

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[14] A. van der Ziel, *Noise* (Prentice Hall, Inc., New York, 1954), p. 210. G. G. McFarlane, Proc. Phys. Soc. (London) **B63**, 802 (1950); E. Keojran and J. S. Schaffer, Proc. Inst. Radio Engrs. **40**, 1456 (1952); R. L. Petritz, Phys. Rev. **87**, 535 (1952); Proc. Inst. Radio Engrs. **40**, 1440 (1952).

[15] J. Evans, Phys. Rev. **57**, 47 (1940); C. C. Klick and R. J. Maurer, Phys. Rev. **81**, 124 (1951).

about half of the data were obtained with the crystal current reversed. In the statistical analysis only the second 20-second interval was used for each reversal in order to assure an equilibrium free of switching transients. The average unbalance voltage for a given interval, when subtracted from the average for the intervals immediately preceding and following, gave the apparent Hall voltage corresponding to a single field reversal. The mean value for all reversals gave the measured Hall voltage. The statistical error in V_y (Table II) is the standard deviation of the mean from the true value.

The most extensive study was carried out on the specially selected low-resistivity crystal 104. Data were obtained for a number of magnetic field strengths and over a wide range of crystal currents. The use of an interpole furnace was excluded by the necessity of obtaining a high magnetic field. However, the crystal temperature was varied over a moderate range (25°C to 230°C) by the Joule heating arising from the crystal current. A separate calibration of the crystal as a resistance thermometer was carried out in the furnace. The resulting data were used to obtain the temperature corresponding to a given crystal current.

B. Results

Hall measurements were made on three boron crystals (numbers 104, 23(*b*), 40). The Hall coefficient R_H in cm^3/coulomb was calculated from $R_H=10^8V_yt/H_zI_x$, where V_y is the Hall voltage (volts), t is the crystal thickness (cm), H_z is the magnetic field (gauss), and I_x is the crystal current (amp). Because the crystals tapered to a relatively small current contact, the Isenberg correction[16] was not important. The standard deviation of R_H (Table II) includes the uncertainties in t and H_z.

Table II summarizes the Hall effect results. Runs 2 through 6 show that the Hall voltage for germanium varied linearly with magnetic field strength. Runs 7 through 23 were made on boron crystal 104 which, like boron crystal 103, was selected for its extremely low resistance (Table I). The Hall coefficient was observed to be independent of the magnitude of the magnetic field or the direction of the crystal current. With increasing crystal current, R_H decreased owing to the heating of the crystal. Runs 12 through 15 showed that the Hall voltage varied linearly with magnetic field strength. Runs 16 through 23 showed the dependence of Hall coefficient upon crystal current, and hence upon temperature. Run 25 was on a typical high-resistivity crystal as shown in Table I and Fig. 2; in this run noise and drift problems were especially serious.

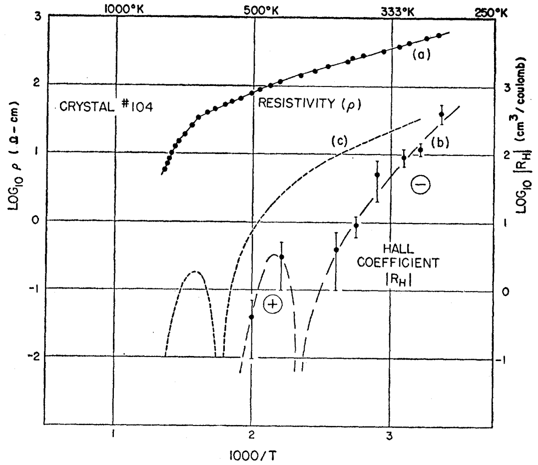

FIG. 3. Resistivity and Hall coefficient of an *n*-type boron crystal.

Figure 3 (curve *b*) shows the dependence of R_H upon absolute temperature (T). The Hall coefficient of crystal 104 was negative at 297°K and, at first, decreased in absolute magnitude as the temperature was increased. With further increase in temperature the Hall coefficient changed sign and remained positive. The data thus indicated that this low-resistivity crystal was an *n*-type semiconductor at room temperature. As the temperature of the crystal was increased, the number of holes increased owing to thermal excitation of electrons from the valence band either to the conduction band or (possibly) to acceptor impurity levels. At high temperatures the numbers of positive and negative charge carriers must approach equality and the small positive Hall coefficient may be interpreted as indicating that the mobility of the holes in boron is greater than the mobility of the electrons. (This conclusion is verified by our thermoelectric measurements.)

The change in sign of the Hall coefficient seems to occur at a temperature much lower than that at which the crystal becomes an intrinsic semiconductor which, according to the resistivity curve in Fig. 3(*a*), is between 600°K and 700°K. One would expect a curve more like like the hypothetical curve (*c*). It is not possible that our method of measuring crystal temperature was this inaccurate. A tentative qualitative explanation could be that an acceptor level as well as donor levels was present in the crystal. If the activation energy for the acceptor level was somewhat greater than that for the donor levels but the number of acceptors was much greater, then a curve similar to that observed might result. An appreciable change of slope observed in the resistivity curve at 430°K could be attributed to this acceptor level.

The Hall-effect measurement of boron crystal 23(*b*) (Table II) is particularly interesting because the Hall coefficient was negative. Originally the resistivity *versus* temperature curve of crystal 23 was typical like that of crystals 40 or 46. As shown in Table II, the Hall coefficient of crystal 40 was positive at 25°C and hence the Hall coefficient of crystal 23 was also presumably positive before the heat treatment. It follows that the

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[16] Isenberg, Russell, and Greene, Phys. Rev. **74**, 1255 (1948); Rev. Sci. Instr. **19**, 685 (1948).

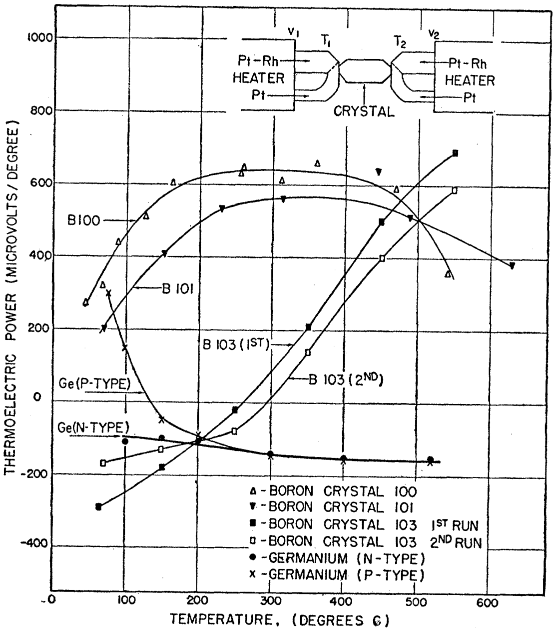

FIG. 4. Thermoelectric power of boron.

application of heat to crystal 23 introduced a large number of ionized donor impurities (or defects). The resulting negative carriers would lower the resistivity and change the sign of the Hall coefficient. In germanium such heat treatment ordinarily increases the number of holes rather than the number of electrons.

IV. AUXILIARY MEASUREMENTS

A. Thermoelectric Effect

The thermoelectric effect in polycrystalline boron was first studied by Taft[17] in 1947 and later by others.[6,7] These experiments indicated that hole conduction predominates over electron conduction. The present work[9,10] on single crystals shows that hole conduction predominates at high temperatures. At low temperatures hole conduction predominates in typical high-resistance crystals but electron conduction may predominate in low-resistance crystals. These qualitative conclusions were verified for over 100 boron single crystals by a very simple test. When a heated tungsten probe was brought into contact with a boron crystal, the typical crystal (e.g., crystal 46) was positive with respect to the tungsten probe as would be expected for hole conduction. The potential differences in the case of boron were approximately five times as large as those observed in an identical test on a crystal of germanium. Boron crystals 103 and 104 were negative with respect to the probe if the probe temperature was low, but positive with respect to the probe if the probe temperature was high.

The experimental arrangement for measuring the thermoelectric power quantitatively is shown in the inset of Fig. 4. The crystal was supported between two heated electrodes each of which consisted of a Pt-PtRh thermocouple. The potential difference $V=(V_2-V_1)$ between the platinum electrodes was positive for the typical *p*-type boron crystal (or for *p*-type germanium) where $T_1>T_2$. The temperature T_2 was held constant and T_1 was varied.

Figure 4 shows the thermoelectric power (dV/dT_1) *versus* temperature (T_1). Typical boron crystals 100 and 101 had resistivity characteristics similar to crystal 46; the low-resistance boron crystal 103 had resistivity characteristics similar to crystal 104 (see Table I and Figs. 2 and 3). The values agree in order of magnitude with the measurements on pyrolytic boron by Taft[17] who found values ranging from 150 to 500 microvolts/degree, and those measurements on polycrystalline boron by Irie, Uno, Yoshida, and Shinohara,[7] who found values up to 180 microvolts per degree. The germanium crystals were comparable in size to the boron crystals and served to test the apparatus. At high temperatures, where the number of holes and number of electrons are practically equal, the thermoelectric power of germanium is always negative. This result indicates that the mobility of the electrons in germanium is greater than the mobility of the holes.[18] On the contrary, at high temperatures, the thermoelectric power of boron is always positive. This result indicates that the mobility of the electrons in boron is less than the mobility of the holes. The change in sign of the thermoelectric power of crystal 103 near 550°K occurs somewhat below the onset of intrinsic conduction near 800°K (Fig. 2). Also, the increase with temperature appears somewhat slow to result from the onset of intrinsic conduction. These data suggest the presence of acceptors as well as donors as tentatively postulated to account for the rather low temperature at which the Hall coefficient changes sign (Fig. 3).

The thermoelectric power of boron crystal 103 was negative at low temperatures and became positive at high temperatures. This observation suggests that the low resistance of this crystal, like the low resistance of crystal 104, was caused by donor impurities. Furthermore, the thermoelectric power became positive at a higher temperature on the second run. This result would be expected if the heating of the crystal during the first run introduced additional donor impurities. The thermoelectric measurements thus confirm the conclusion suggested by the resistivity and Hall data, that the heating of boron crystals to several hundred degrees centigrade reduces the low-temperature resistivity by introducing additional donor impurities.

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[17] E. Taft (unpublished results kindly communicated by L. Apker, General Electric Laboratories, Schenectady, New York).

[18] V. A. Johnson and K. Lark-Horovitz, Phys. Rev. 92, 226 (1953).

B. Rectification

Boron crystal 46 (a typical crystal) was mounted with five electrodes as shown in Fig. 1 of reference 11. The resistance was measured (at 1.5 volts) with various combinations of the five electrodes taken two at a time. Rectification was observed between the large area current electrodes and the pointed voltage probes; none was observed between current electrodes or between voltage probes. The direction of easy (positive) current flow was from the large contacts to the points. The measured resistances were about 1000 megohms for difficult flow and about 500 megohms for easy flow. Each of the contacts was then "formed" by connecting it several times to the high-voltage terminal of an automobile spark coil. The forming operation reduced the contact resistance in many cases by a factor of two or more. Rectification effects were absent when formed electrodes were used.

In all cases in which rectification was observed, the lowest resistance was observed when the point contact was the negative electrode. That is, the direction of easy flow for positive charge carriers at the point contact was from the crystal to the electrode. This behavior is characteristic of *p*-type germanium or silicon. Since we know from Hall and thermoelectric measurements that typical crystals are *p*-type, it may be concluded that in boron as in germanium and silicon, the charge carriers must go over the rectification barrier rather than tunnel through the barrier.[19]

C. Photoconductivity

Photoconductivity in crystalline boron has been studied by Freymann and Steiber[4] and by Lagrenaudie.[6] In our case a decrease in resistance (at 1.5 volts) with exposure to light was observed in each of eight single crystals. Reduction in resistances ranging from 10% to 50% was observed. A calculation showed that the observed reduction could not be attributed to radiant heating of the crystal. Furthermore, the decrease in resistance was unaltered by removal of the infrared radiation from the white light used. No reduction in resistance was observed when the boron crystal was exposed to x-rays, and a small reduction was observed with ultraviolet radiation.

V. PROPERTIES OF CHARGE CARRIERS

A. Activation Energies

An activation energy (ϵ) in a semiconductor may be defined in terms of the resistivity ρ at temperature T by the equation $d\ln\rho/d(1/T)=\epsilon/k$. If the slope of the $\ln\rho$ *versus* $1/T$ curve varies continuously with temperature, the value of ϵ at one particular temperature is not likely to be an easily interpretable property of the intrinsic material. Its value depends largely upon the densities and kinds of impurities and the relative importance of impurity scattering compared to thermal scattering. Figure 2 shows (below 800°K) that ϵ is dependent upon the temperature, purity, and past history of the crystal. For a typical crystal, such as boron crystal 46, the activation energy varies from 0.79 electron volt at 800°K to 0.25 ev at 200°K. The entire curve can conceivably be obtained from four straight lines having activation energies of 0.79 ev, 0.50 ev, 0.34 ev, and 0.25 ev. The 0.79-ev activation energy is almost certainly related to the intrinsic energy gap (E_g) between the valence and conduction bands because the high-temperature region of the curve is straight for three decades. If the curvature arises mainly from impurities, it appears that at least three energy levels are required. The level most effective in contributing carriers at 300°K must be an acceptor level since both Hall measurements and thermoelectric power measurements on typical crystals showed that hole conduction predominated at room temperature. On the other hand, special crystals (such as 103 and 104 selected for their unusually low resistivity at room temperature) had activation energies as low as 0.06 ev. Hall and thermoelectric measurements showed that these activation energies corresponded to donor levels. Likewise, the low activation energies (at 300°K) of crystals 22 and 23, observed after heat treatment, correspond to donor levels.

It is desirable to evaluate the intrinsic energy gap (E_g) between the filled and conduction bands. The intrinsic range appears to exist in boron single crystal, at temperatures above 800°K. Figure 2 shows that, above 800°K, ϵ is independent of the temperature, purity, and past history of the boron crystal. This activation energy is intrinsic to boron and has a value of 0.79 ev. However, the deduction of E_g from conductivity data alone is subject to some uncertainty because of the dependence of carrier mobility upon temperature. An evaluation based on the most natural assumption will be presented. In the intrinsic range it is reasonable to assume (1) that the number of electrons (n_e) is equal to the number of holes (n_h), and (2) that the predominant scattering mechanism for the charge carriers is thermal scattering by acoustical modes (mobilities proportional to $T^{-\frac{3}{2}}$). Free-electron theory then shows that the energy gap is 2(0.79 ev) or 1.58 ± 0.05 ev. For an energy gap this large, the exponential term in the conductivity is so strong that the numerical value of E_g would not be altered appreciably even if the temperature dependence of the mobility were somewhat different from $T^{-\frac{3}{2}}$. For example, the complex crystal structure of boron (50 atoms per unit cell) suggests that thermal scattering by optical modes could be significant and such scattering could give a different dependence of mobility upon temperature. Combinations of scattering by acoustical modes ($\mu\sim T^{-\frac{3}{2}}$) and by possible optical modes ($\mu\sim T^{-(n+\frac{3}{2})}$) were used in an attempt to fit the typical resistivity curve (Fig. 2)

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[19] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1946), p. 180.

with the form $\ln\rho = (E_g/2kT) + \ln(A + BT^n)$. However, no fit is possible with reasonable values of E_g and either positive or negative values of n.

Our value for E_g is substantially higher than that reported by most other investigators, all of whom have used polycrystalline samples rather than single crystals. Impurities, crystal defects, or surface barriers reduce the activation energy. Furthermore, a low value of E_g may be obtained if the activation energy is measured at temperatures lower than 800°K. Hence a large E_g is likely to be more trustworthy than a smaller value—especially if single crystals are used. Low values for E_g determined thermally have been reported by Moss[5] (1.0 to 1.25 ev), Jacobsmeyer *et al.*[8] (0.3 to 0.9 ev), and Lagrenaudie[6] (1.2 ev). Higher values have been obtained at high temperatures (200–1000°K) by Uno, Irie, Yoshida, and Shinohara[7] (1.44 ev) and by Taft[17] (1.5 ev from his graph).

Lower values of E_g (1.0 to 1.25 ev) have been obtained from optical absorption and photoconductivity data taken at room temperature.[4,5,20] Direct comparison of thermal and optical activation energies is difficult. However, the experimental evidence shows that the thermally determined energy gap is greater (rather than less[21]) than the optically determined energy gap.

B. Mobilities

The Hall measurements at 500°K (Sec. IIIB) and the thermoelectric measurements at 800°K (Sec. IVA) have indicated that at high temperatures the hole mobility is greater than the electron mobility provided that the specimens are in the intrinsic range. Quantitative mobility estimates can also be made.

The Hall mobility of electrons at 300°K in the low-resistivity crystal 104 can be estimated from the data in Fig. 3. At this temperature the Hall coefficient is negative and we shall assume that the number of holes is negligible. The electron mobility at room temperature is then given by $\mu_e = -(8/3\pi)(R_H/\rho)$. At 300°K, $R_H = -400$ cm^3/coulomb, $\rho = 610$ ohm-cm, and $\mu_e = 0.6$ cm^2/volt-sec. For crystals 24(*b*) at 300°K, $R_H = -2650$ cm^3/coulomb, $\rho = 2500$ ohm-cm, and $\mu_e = 0.9$ cm^2/volt-second. A weighted mean for the mobility of the electrons in these particular boron crystals is estimated to be $\mu_e = 0.7 \pm 0.3$ cm^2/volt-second.

The Hall mobility of the holes at room temperature is not easily obtained. None of our low-resistivity crystals were *p*-type impurity semiconductors and hence the mobility of the holes could not be found from a single low-temperature Hall measurement on a low-resistivity sample. The apparent anomalous temperature dependence of the Hall coefficient for crystal 104 is difficult to understand quantitatively. For this reason, and also because the measurements depended on a single specimen, it was considered inadvisable to attempt to calculate μ_h from the temperature dependence of the Hall coefficient for crystal 104. However, we can estimate the hole mobility from our single Hall measurement at 300°K (on typical high-resistivity crystal 40) if we assume that the crystal is a *p*-type semiconductor at 300°K with $n_e = 0$. In this case, $\mu_h = (8/3\pi)(R_H/\rho) = (8/3\pi)(2.8\times10^5/1.7\times10^6) = 0.2 \pm 0.15$ cm^2/volt-sec. This assumption predicts $\mu_h < \mu_e$ within rather large errors: $\mu_e - \mu_h = 0.5 \pm 0.3$ cm^2/volt-sec. However, we have shown (Secs. IIIB and IVA) that $\mu_h > \mu_e$ at high temperatures and presumably also at room temperature. It is most likely, therefore, that n_e is not zero as we assumed and that donors as well as acceptors contribute charge carriers at 300°K.

The conclusions to be drawn are (a) that the mobility of the holes is greater than the mobility of the electrons and (b) that the mobilities are very low compared to those found in most semiconductors. Such low mobilities may be caused by defects in our particular crystals. It is also possible that the low mobilities arise from thermal scattering by optical modes associated with the complicated crystal structure of boron. Such low mobilities will prevent boron from being useful in many applications of semiconductors. In addition it is, unfortunately, not likely that single crystals of boron could be used as conduction counters for detecting neutrons by the $B^{10}(n,\alpha)Li^7$ reaction.

C. Densities

The Hall coefficient of crystal 104 at 300°K was -400 cm^3/coulomb. If the crystal is assumed to be in the impurity range with $n_h = 0$, then $n_e = 3\pi/8eR_H = 1.8\times10^{16}$ cm^{-3}. It is not possible to make a reliable estimate of the carrier densities in a typical crystal at any temperature. At high temperatures there is no Hall data, and the uncertainties regarding the scattering process and effective masses preclude a worthwhile calculation from the present measurements. Since, at low temperatures, the crystal is unlikely to be intrinsic or to have only positive carriers, a calculation from the Hall data at 300°K is impracticable. For the same reasons, calculations of effective masses from these experimental measurements are not feasible.

APPENDIX

The Ettingshausen effect is a possible source of error in a Hall measurement on a semiconductor. This error was estimated for our crystals. The fractional difference (x) between the adiabatic (R_a) and isothermal (R_i) Hall coefficients is a good measure of the error. Johnson and Shipley[22] have computed $x \equiv (R_a - R_i)/R_i$ for semiconductors. A very pessimistic thermal conductivity of 10^{-2} watt cm^{-1} deg^{-1} was used in the apparent absence

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[20] N. Morita, J. Sci. Research Inst. Tokyo 48, 8 (1954).

[21] Reference 19, p. 161.

[22] V. A. Johnson and F. M. Shipley, Phys. Rev. **90**, 523 (1953). It appears that a typographical error has placed an extra power of e in Eq. (41) of this reference. The data in their Table VI are consistent with the corrected equation.

of data in the literature; the true value is probably closer to one watt cm^{-1} deg^{-1}. The largest possible value of $|x|=5\times10^{-10}$ was found for crystal 40 by assuming intrinsic conductivity at 300°K. For crystal 104 the largest $|x|=4\times10^{-5}$ was obtained when impurity scattering in the low temperature region was arbitrarily assumed, and an even smaller value was found for lattice scattering.

A check on these calculations may be obtained by means of a phenomenological argument. It may be shown that the fractional Ettingshausen error in the Hall voltage is equal to QP/R_i, where Q is the thermoelectric power of the semiconductor-metal junction and P is the Ettingshausen coefficient. The classical free-electron theory for a single carrier gives $R_i/P=4k/e=345$ microvolts/deg if the thermal conductivity is all electronic.[23] To take into account the lattice conductivity this value must be multiplied by the ratio (r) of total thermal conductivity to electronic thermal conductivity.[24] A most pessimistic estimate of the error in boron was made by considering crystal 104 (Fig. 3) at 500°K. The Wiedemann-Franz ratio of $2k^2/e^2$ (classical statistics) was used to estimate the electronic contribution to the thermal conductivity. This estimate gave $r=10^5$. Using $Q=600$ microvolts/deg from Fig. 4, we found the largest fractional Ettingshausen error to be the order of 2×10^{-5} for crystal 104 (and many orders of magnitude smaller for crystal 40). A formula[25] for P which takes into account carriers for both signs gives essentially the same results.

It is concluded that for our Hall measurements the fractional error from the Ettingshausen effect cannot possibly exceed 10^{-4} no matter what type of scattering and conductivity are assumed. The smallness of the error is a direct consequence of the fact that the scarcity of carriers produces a high ratio of lattice thermal conductivity to electronic thermal conductivity.

ACKNOWLEDGMENT

We wish to thank R. D. Redin for a helpful study of classical thermomagnetic phenomena.

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[23] A. Sommerfeld and N. Frank, Revs. Modern Phys. 3, 1 (1931).

[24] L. Stilbans, Zhur. Tekh. Fiz. 22, 77 (1952) (in Russian), abstracted in Physics Abstr. 55, Sec. A, No. 8177 (1952).

[25] A. Johnson and K. Lark-Horovitz, Phys. Rev. 73, 1257(A) (1948).

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Thermal Conductivity of Indium Antimonide

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The thermal conductivity of indium antimonide of varying purity has been measured by a comparative method from 40°C to 425°C. The electronic component of the conductivity has been calculated for each specimen and hence the lattice thermal conductivity has been deduced. Within the limits of experimental error InSb appears to behave according to conventional theory.

USING a comparative method previously described,[1] measurements of the thermal conductivity of single crystals of indium antimonide of varying purity have been made from 40°C to 425°C. The results shown in Fig. 1 represent the average of several measurements on each sample and have an estimated accuracy of ±10%.

In the temperature range considered, specimens A and C were essentially similar to specimens $P-N-A_2$ and $P-N-C_2$ for which electrical conductivity and thermoelectric power data have already been given.[2] Specimen B was "n"-type and contained 10^{17} extrinsic electrons/cc. Specimens A and B are weakly degenerate over the temperature range and specimen C strongly so near room temperature. The kinetic energy transport K_E in the three samples has been calculated according to the expression

$$K_E=S(k/e)^2\sigma T,$$

where the symbols have their usual meaning and S is a

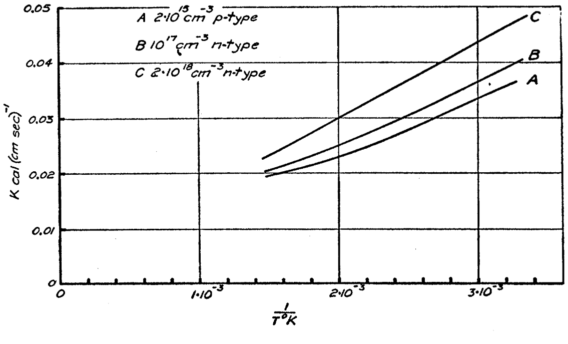

FIG. 1. Thermal conductivity of indium antimonide.

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[1] A. D. Stuckes and R. P. Chasmar, *Report of the Meeting on Semiconductors* (The Physical Society, London, 1956), p. 119.

[2] Antell, Chasmar, Champness, and Cohen, *Report of the Meeting on Semiconductors* (The Physical Society, London, 1956), p. 99.