

THERMOELECTRIC POWER AND ELECTRICAL RESISTIVITY OF MINERALS*

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ABSTRACT

The thermoelectric power and the electrical resistivity of a relatively extensive group of minerals was determined. These properties were measured on various cut and ground samples of the same specimen to show possible correlation. Different samples of the same mineral were used to establish variations in the magnitude of the electrical properties. The data obtained show considerable variations, probably due to the presence of impurities, but they establish the order of magnitude of the electrical properties. The data should be helpful in the study of pure synthetic semi-conductors and in the understanding of the electronic properties of these materials.

INTRODUCTION

A large group of minerals are semi-conductors, prepared by nature, generally impure, but readily available. Considerable experimental work has been carried out in determining the electrical resistivity of minerals and rather scattered efforts were made in measuring their thermoelectric power. A knowledge of the electrical resistivity and the thermoelectric power of minerals or pure synthetic semi-conductors are necessary adjuncts in the study of the electronic properties of materials.

Rather large variations exist in the resistivity of different specimens of the same mineral, which may be attributed to the presence of heterogeneous or non-stoichiometric impurities. The simultaneous determination of the thermoelectric power and the resistivity on several cut and ground samples of the same mineral specimen, should permit a definite correlation of these properties. Determinations on different specimens of the same mineral should be helpful in establishing order of magnitude correlations.

Comparison of metallic arsenides, sulfides, oxides, etc., should establish further correlations between the chemical nature of these materials and their electrical properties.

The possible use of minerals or their synthetic varieties, as rectifiers, thermocouples, or other electronic devices depends upon a more exact knowledge of their electrical properties.

1. REVIEW OF THE LITERATURE

The electrical resistivity of polished mineral specimens has been determined by Harvey (21). He used the four electrode method (two potential

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drop leads, between two current supplying leads). His method did not permit the exact determination of the specific electrical resistivity, the values are relative, giving the order of magnitude variations. Harvey used more than 2,000 samples and found that the electrical resistivity of different specimens of the same mineral varied considerably; the previous literature has been summarized by Harvey.

Thermoelectric Power. The various "thermoelectric series" of minerals established by Seebeck (37), Becquerel (5), Hankel (19), Marbach (28), Bunsen (9), Flight (14), Stefan (40), Schrauf and Danna (38), Kundt (26), Iljew (23), and others can be regarded as qualitative indications.

Various specimens of the same mineral differed, often markedly, in the thermoelectric power value. Various specimens sometimes gave positive or negative values and in some cases positive and negative spots could be located on the same specimen. Variations of positive and negative spots have been studied by Groth (18), Hankel (20), and Rose (35). Kundt (26) devised a method to differentiate the thermoelectrically positive and negative regions of a specimen. The mineral was heated slightly and dusted with a mixture of powdered sulfur and minium; the sulfur became attached to the positive regions, while the minium adhered to the negative spots, revealing them in yellow and red colors.

Quantitative data of thermoelectric power determinations on minerals can be found in various Handbooks (Chapters by Laski (27) and Meissner (29), in the International Critical Tables, in Landolt-Bornstein's and other tables). Some of these data give merely an order of magnitude indication. It appeared advisable to collect the data from the literature, which are summarized in Table 1. In this table the thermoelectric power values are shown in microvolt/ $^{\circ}$ C. with copper as the reference metal. Most of the experimental data were obtained with cold junctions at 0° C. (or 20° C.) and the hot junction at 100° . The thermoelectric power varies with the temperature and therefore the range of the measuring temperature should be noted.

The sign of the thermoelectric power is based upon a conventional agreement; material *A* is positive against a reference material *B*, if the thermal current flows in the same direction as the conventional electric current does when the circuit is closed. Some of the early papers did not follow this convention and therefore the original papers have been carefully scrutinized and whenever possible the sign convention has been ascertained.

From an examination of Table 1 it is obvious that various specimens of the same mineral show considerable variations in magnitude and may even differ in sign. The existence of positive and negative spots in the same specimen has been established. The reason for the positive and

TABLE 1. THERMOELECTRIC POWER (e) OF MINERALS
(REVIEW OF THE LITERATURE)

<i>Material</i>	e microvolt/° C. ref. Cu	<i>Temp.</i> °C	<i>Reference</i>
ARGENTITE Ag ₂ S	-910	20-100	1888 Chaperon (10)
	-285	400	1888 Chaperon (10)
fused	70	20-100	1930 Reinhold (34)
CHALCOCITE Cu ₂ S	181 to 327	20-100	1866 Becquerel (6)
fused	340	20-100	1866 Becquerel (6)
fused	54	20-100	1932 Waibel (42)
fused	100	20-100	1930 Reinhold (34)
BORNITE Cu ₅ FeS ₄	405	0- 25	1929 Ogawa (31)
GALENA PbS	-290 to 340	20-400	1888 Chaperon (10)
	-250	0-100	1900 Abt (1)
	160	0-100	1913 Streintz (41)
	-248	0- 25	1929 Ogawa (31)
	-490	20-200	1931 Fujii (16)
	-210		1932 Waibel (42)
	150		1933 Rupp (36)
	max. 2100	20-100	1935 Dean (13)
CHALCOPYRITE CuFeS ₂	-280	0-100	1900 Abt (1)
	-425	0- 25	1929 Ogawa (31)
PYRRHOTITE Fe _{1-x} S	14	0-100	1900 Abt (1)
	-20	0-100	1909 Koenigsberger (24)
MILLERITE NiS	0	0-100	1900 Abt (1)
COVELLITE CuS thin film	7	20-100	1905 Baedeker (3)
STIBNITE Sb ₂ S ₃	1600		1913 Planck (33)
BISMUTHINITE Bi ₂ S ₃ fused	-80		1938 Hochberg (22)
PYRITE FeS ₂	185	0-100	1900 Abt (1)
	-115	20-200	1931 Fujii (16)
	130 to 210	0-100	1911 Koenigsberger (25)
	-344 to 524	0- 25	1929 Ogawa (31)
	-180		1932 Waibel (42)
MARCASITE FeS ₂	280	20-200	1931 Fujii (16)

TABLE 1—Continued

<i>Material</i>	$\frac{e}{\text{microvolt}/^\circ\text{C.}}$ ref. Cu	<i>Temp.</i> °C	<i>Reference</i>
ARSENOPYRITE FeAsS	-265	20-200	1931 Fujii (16)
	-242	0-237	1888 Backstrom (2)
MOLYBDENITE MoS ₂			(11)
15 specimens	700 to -1000		1924 Coblenz (12)
	460 to 730	20-100	1914 Gottstein (17)
	560		1921 Miller (30)
8 specimens	175 to -720	0-200	1909 Pierce (32)
	-1400	0- 25	1929 Ogawa (31)
	-750		1932 Waibel (42)
pressed	800		1938 Hochberg (22)
ZINCITE ZnO	-650	0- 25	1929 Ogawa (31)
fused	-720	320-400	1914 Bidwell (7)
sintered in air	839	550-650	1933 Baumbach (4)
sintered in H ₂	510	550-650	1933 Baumbach (4)
crystal	400		1935 Fritsch (15)
crystal heated in H ₂	200		1935 Fritsch (15)
HEMATITE Fe ₂ O ₃	-660	20-400	1888 Chaperon (10)
	470	20- 50	1909 Koenigsberger (24)
	300	0-237	1888 Backstrom (2)
fused	-700	500-550	1916 Bidwell (7)
oxidized wire	430	20-700	1915 Brown (8)
ILMENITE FeTiO ₃	-130	20- 50	1909 Koenigsberger (24)
PYROLUSITE MnO ₂	-124	0-100	1900 Abt (1)
MANGANITE MnO(OH)	190	20- 50	1909 Koenigsberger (24)
	265	20- 50	1911 Koenigsberger (25)
PSILOMELANE	-3200	0- 25	1929 Ogawa (31)
MAGNETITE Fe ₃ O ₄	55	20- 50	1909 Koenigsberger (24)
fused	-60		1914 Bidwell (7)

negative variations has been attributed to impurities. In molybdenite the difference may have been due to the presence of oxide as impurity, according to Coblenz (12). Ogawa found that argentiferous galena has a positive thermoelectric power (31) as compared to the usual negative value.

The thermoelectric power varies with crystal orientation. There are,

however, insufficient data available to permit a quantitative correlation for various materials.

The synthetic materials, or pressed and sintered samples, sometimes show similar results to the minerals, but, depending upon the method of preparation, may differ considerably.

A review of the literature shows that the available data are not sufficient and considerable work is required to collect additional data.

2. EXPERIMENTAL ARRANGEMENT

The mineral specimens were obtained from the collection of the Geol-

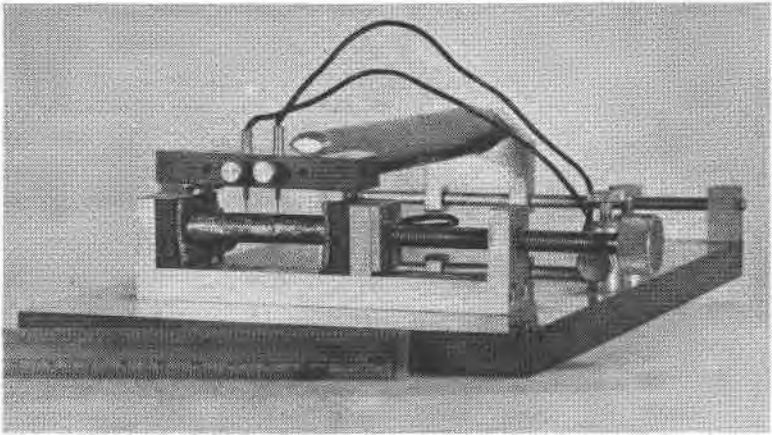


FIG. 1. Convenient resistivity apparatus

ogy Department of the Massachusetts Institute of Technology, or they were purchased from Ward's Natural Science Establishment. Many of the specimens were polished sections, or they were cut to prismatic shape.

The electrical resistivity (specific electric resistance) can be determined only on samples cut to cylindrical or prismatic form. The four electrode method was used, with the specimen clamped between two current supplying blocks. Two needle electrodes were pressed against the surface of the specimen and connected to a potentiometer to measure the voltage drop between them. A convenient apparatus used in these measurements is shown in Fig. 1. The needle electrodes can be moved along the length of the specimen exploring possible variations, which may be present due to cracks, or possible rocky inclusions.

The following data are established:

ρ specific resistance (resistivity), Ohm. cm.
I current flowing through specimen, Amp.
E voltage drop between needle electrodes, Volt.
L distance between needle electrodes, cm.
s cross section of sample, cm².

$$\rho = \frac{E \cdot s}{I \cdot L} \text{ (Ohm. cm)}$$

The current was supplied from several large dry cells connected in parallel to minimize fluctuations. The current was measured with an ammeter; for specimens of higher resistivity a milli or microammeter was

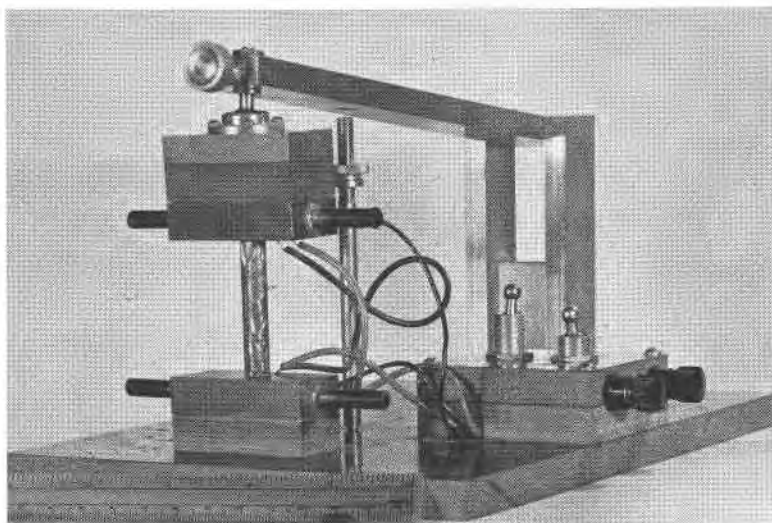


FIG. 2. Apparatus for measuring thermoelectric power

used. The voltage drop was measured with a potentiometer. The measurements were made at room temperature (around 20–25° C.). It was found that the resistivity of most minerals varied considerably, even on samples cut from the same mineral specimen. Generally the values agreed within 10 per cent when measured on the same specimen. In some cases greater accuracy could be obtained, which is indicated in the results.

Thermoelectric power. The usual method of determining the thermoelectric power was followed, using the convenient apparatus shown in Fig. 2. The specimen was clamped between two copper blocks, the top one was heated with steam, the lower one cooled with circulating water. A differential thermocouple was attached to the two blocks to permit

TABLE 2

	<i>Mineral</i>	e Thermoelectric power, ref. Cu microvolt/° C.	ρ Specific resistance Ohm. cm.
1113	Huntelite Ag ₃ As Lake superior, polished	-33	low
2112	Tetradymite Bi ₂ Te ₂ S New Mexico Texas	HR -63	low
212	Nagyagite Pb ₆ Au(TeSb) ₄ S ₆₋₈ ? Nagyag, Transylvania	-64	low
213	Mohawkite Cu ₃ As Michigan Cobalt, Ont. Polished	-30 -33 -30	low low low
2131	Algodonite Cu ₆ As Lake superior, polished	-68	low
2132	Domeykite Cu ₃ As Portage Lake Calumet, Mich.	-15 -15	low low
2311	Argentite Ag ₂ S Sonora, Mexico	-1000	high
2321	Chalcocite Cu ₂ S Butte, Mont. Sonora, Mexico Cornwall Bristol, Conn. Bristol, Conn. Thuringia	265 495 75 190 250 70	0.06 0.27 low low low low
2322	Stromeyerite AgCuS Ontario Saxony Arizona	-400 150 HR	10 ⁵ med.
243	Bornite Cu ₅ FeS ₄ Butte, Mont. Sangerhausen, Germany Silverton, Colo. Bisbee, Ariz.	260 40 100 365	0.031 0.016 0.007 0.13

TABLE 2—Continued

<i>Mineral</i>		<i>e</i> Thermoelectric power, ref. Cu microvolt/° C.	<i>p</i> Specific resistance Ohm. cm.
Bornite & Chalcocite			
	Butte, Mont.	320	0.10
	Butte, Mont. (4 specimens)	320	low
Bornite & Covellite			
	Cornwall	150	low
	Polished	130	low
	Polished	340	low
252	Rickardite Cu_4Te_3 Polished	-14	low
2611	Galena PbS		
	Mies, Bohemia	-450	3.0 to -6
	Northport, Wash.	-300	0.08
	Aspen, Colo., Argentiferous	+370 to -450	0.35
	Gregory Mine, Colo.	-150 to -250	0.3 to .22
	Hartz, Germany	-110	0.007 to .0041
	Siebengebirge, Germany	-295 to -320	120
	Wallace, Idaho, Argentiferous	-260	200
	Galena, Ill.	+275 to -220	0.035
	Galena, Kan.	-50 to -260	0.026
	and Chalcopyrite		
	Butte, Mont.	-380	12
	Galena		
	De Soto Mine, Nev.	-295	low
	Franklin, N. J.	-300	low
	New South Wales	-210 to -250	0.02 to .36
	Monte Poni, Sardinia	-220	0.02
	Zeehan, Tasmania	-300	20
	Harvard Collection		
	No. 81742	-370	low
	87947	-345	low
	81749	-385	low
	81731	-360	low
	81718	-120 to +40	+ - spots
	Joplin	-190	+ - spots
	Joplin Roach Mine	-440	+ - spots
	Joplin	-220	+ - spots
	St. Eulalia, Mexico	-370	+ - spots
	Salchendorf, Westfalen	-250	+ - spots
	Leadville, Colo.	-200	+ - spots
	Galena	-200 to -260	+ - spots
	Argentiferous	+85	+ - spots

TABLE 2—Continued

	<i>Mineral</i>	<i>e</i> Thermoelectric power, ref. Cu microvolt/° C.	<i>ρ</i> Specific resistance Ohm. cm.
2614	Alabandite MnS Nagyag, Hungary	HR	
2621	Sphalerite ZnS Ottawa County, Okla. (excellent heat con- ductor)	900	high
	Bingham, Utah, 3 samples	180	med.
2622	Metacinnabar HgS, polished	90	low
2623	Tiemannite HgSe Utah, polished	-43	low
2624	Coloradoite HgTe Kalgoorlie, Australia	-27	low
	Kalgoorlie, polished	-30	low
2631	Chalcopyrite & bornite CuFe ₂ S ₄ South Australia	260 to 210	2.0
2631	Chalcopyrite with quartz Felsöbánya, Rumania	-310 to -410	low
2631	Chalcopyrite Cu ₂ Fe ₂ S ₄ Rouyn District	-270 to -320	0.43
	Rouyn District	-365	0.032
	Cornwall, Pa.	-340	0.8
	Chester County, Pa.	-290 to -390	0.24
	Ellenville, N. Y.	-405	0.026
	Butte, Mont.	-60 to -170	0.036
	Cornwall, England	-100 to -170	1.7
	Leadville, Colo.	-350	0.04
	Larimer County, Colo.	-160 to -260	0.8
	Gilpin County, Colo.	-360	low
	Cochise County, Ariz.	-360 to -460	0.7 to .37
	Massive Crystals, pure	-400	0.042
	Polished	-380	low
	Harvard Collection		
	No. 80880	-345	low
	82081	-345	low
	Highly twinned	-80 to -230	low
	Freiberg, polished	-290	low
	Westmoreland, Brit.	-230	low
	Quebec	-170	low
	Single crystal, pure	-250	low

TABLE 2—Continued

	<i>Mineral</i>	<i>e</i> Thermoelectric power, ref. Cu microvolt/° C.	<i>p</i> Specific resistance Ohm. cm.
2632	Stannite $\text{Cu}_2\text{FeSnS}_4$		
	Zinnwald, Bohemia	210	300
	Oruru, Bolivia	370	med.
	Zeehan, Tasmania	60	med.
	Tolwing N.S.W. (2)	60	med.
2641	Wurtzite ZnS , polished	HR	
2642	Greenockite on sphalerite CdS		
	Hanover, Grant County, N. M.	HR	10^6
	5 samples	HR	
2651	Pyrrhotite Fe_{1-x}S		
	Frederick County, Maryland	60	0.10
	Standish, Me.	1	low
	Sudbury, Ont.	-14	low
	Cold Springs, N. Y.	0	low
	Troilite Fe_{1-x}S		
	Del Norte County, Calif.	-37	low
	Calif., polished	-13	low
	Benholm, Ont.	-11	low
2653	Nicolite NiAs		
	Germany, polished	-34	low
2655	Millerite NiS		
	Lancaster, Pa., 2 samples	-22	low
	Polished	-25	low
2656	Pentlandite $(\text{Fe}, \text{Ni})_9\text{S}_8$, polished	-25	low
	In pyrrhotite, Worthington, Ontario	11	0.0007
266	Cubanite CuFe_2S_3		
	With chalcopyrite, Pinar del Rio, Cuba	-100 to -160	0.035
	Polished	-70 to -10	low
2681	Covellite CuS		
	Butte, Mont., 5 specimens	-10	low
269	Cinnabar HgS		
	Aleknagik, Alaska	HR	
26.10	Realgar AsS		
	Manhattan, Nev.	HR	
	Polished	HR	

TABLE 2—Continued

	<i>Mineral</i>	<i>e</i> Thermoelectric power, ref. Cu microvolt/° C.	<i>ρ</i> Specific resistance Ohm. cm.
2711	Linnaeite Co_3S_4 Missouri, 2 samples	-10 + spots -170	low low
2714	Violarite Ni_2FeS_4 Polished	-240	low
2715	Polydymite Ni_3S_4 Algoma, Ont. Sudbury, Ont., 2 samples Polished	-22 -20 -20	low low low
281	Orpiment As_2S_3 Saxony	HR	
	Stibnite Sb_2S_3 Sevier County, Ark. Iyo, Japan 6 samples	HR HR HR	
2822	Bismuthinite Bi_2S_3 Llallagua, Bolivia	-200	high
2911	Pyrite FeS_2 No name Yechigo, Japan Isle of Elba Leadville, Colo. Harvard Coll. #82107 92621 82114 88935 82097 Single crystals Distorted crystals Bingham, U. concretion Bingham, U. concretion Newfoundland concretion Elba crystal Mineral Point, Wis. Sandy Run, Pa.	-100 to +300 -120 to +140 -35 to -70 +220 to +455 -40 -280 -70 to -90 -120 to -290 -96 -10 -90 70 150 160 20 to 110 210 50	14 2.6 0.005 1.5 low low low low low low low low low low low low low low
2912	Bravoite $(\text{Fe}, \text{Ni})\text{S}_2$ polished	290	low
2915	Hauerite MnS_2 Raddusa, Italy	HR	

TABLE 2—Continued

	<i>Mineral</i>	ϵ Thermoelectric power, ref. Cu microvolt/° C.	ρ Specific resistance Ohm. cm.
2921	Cobaltite CoAsS Saxony	-40	low
2922	Gersdorffite, NiAsS Ontario, polished	-20	low
2931	Loellingite FeAs ₂ Sweden, polished	-78	low
	Edenville, N. J.	-77	low
	Paris, Me.	-88	low
2932	Safflorite (Co, Fe)As ₂ , polished	-70	low
2933	Rammelsbergite NiAs ₂ , polished	-49	low
	Cobalt, Ont. (2 samples)	-37	low
	Brandt, Saxony	-80	low
	Schladnung, Austria (2)	-84	low
294	Marcasite FeS ₂ Ottawa County, Oklahoma	385 to 770	med.
	Joplin, Mo.	192	low
	Osseg, Bohemia	140	low
	Nagyag, Hungary	170	low
	Polished	120	low
2951	Arsenopyrite FeAsS Jardine, Mont.	-245	0.7
	Anglesea Twp., Ontario	-250	0.7
	Obira, Bungo, Japan	-295	0.08
	Freiburg, Saxony	-140	low
	Nova Scotia	-150	low
	Skykonish, Ash.	-100	low
	Cascade Mountains	-165	low
2952	Glaucodot (Co, Fe)AsS Hakanspoda, Sweden	-55	low
2961	Molybdenite MoS ₂ Santa Cruz County, Ariz.	-570	10
	Lyndoch, Ontario	460	med.
	Harvard Coll. 81617	80 to 490	med.
	91575	240 to -340	+ - spots
	Haddam County	-480	+ - spots
	Haddam County, polished	-430	+ - spots

TABLE 2—Continued

	<i>Mineral</i>	\bar{e} Thermoelectric power, ref. Cu microvolt/° C.	$\bar{\rho}$ Specific resistance Ohm. cm.
2962	Tungstenite WS ₂ Utah, polished	HR	
2973	Sylvanite (Au, Ag) Te ₄ Cripple Creek, Colo.	-50	low
2.10.11	Skutterudite (Co, Ni)As ₃ South Lorraine, Ont.	HR	
2.10.12	Smaltite (Co, Ni)As _{3-x} Schwarzenberg	-30	low
2.10.14	Chloanthite (Ni, Co)As _{3-x} Saxony	-51	low
2.10.2	Patronite Minasragra, Peru Polished	-130 HR	high
3112	Pearcite (AgCu) ₁₆ As ₂ S ₁₁ , polished	HR	
312	Polyargyrite 12(Ag ₂ S)Sb ₂ S ₃ Polished Saxony	-140 HR HR	high
314	Stephanite Ag ₅ SbS ₄ Brand, Saxony Polished	HR HR	
3211	Pyrargyrite Ag ₃ SbS ₃ Zacatecas Guanajuato, Mexico	HR 330	high
3212	Proustite Ag ₃ AsS ₃ Polished, 2 samples	HR	
3241	Tetrahedrite (CuFe) ₁₂ Sb ₄ S ₁₃ Freiberg With pyrite, Bingham, U. With chalcopyrite, Australia With Ag, Talache, Idaho	HR HR -5 80 to 250	low low
3241	Tetrahedrite (argentiferous) With siderite, Coeur D'Alene, Idaho	490	37

TABLE 2—Continued

	<i>Mineral</i>	<i>e</i> Thermoelectric power, ref. Cu microvolt/° C.	<i>ρ</i> Specific resistance Ohm. cm.
3242	Tennantite $3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_3$		
	Utah, polished	310	low
	Bingham, Utah	240	low
	Butte, Mont.	240	low
	Cornwall	190	low
	Braden Mine, Chile	270	low
3312	Germanite (Cu, Ge)(S, As) Polished	-80	low
3321	Famantinite 3CuSbS_4		
	Famatina, Argentina	400 to 560	210
	Famatina, polished	210	med.
3322	Enargite Cu_3AsS_4		
	San Juan Dist., Colo.	465	1.7
	Cerro de Pasco, Peru	325	0.19
	Peru	0 to 100	4.4
	Butte, Mont., polished	410	low
	Butte, Mont.	190	low
	Butte, Mont., Badger vein	300	low
	Butte, Mont., large crystals	420	low
	Tintic, Utah	300	low
	Peru	370	low
335	Geocronite $\text{Pb}_5(\text{Sb}, \text{As})_2\text{S}_8$ Polished	-300	med.
336	Gratonite $\text{Pb}_9\text{As}_4\text{S}_{15}$ Cerro de Pasco, Peru	HR	
339	Guitermanite $\text{Pb}_{10}\text{As}_6\text{S}_{19}$ Colorado	HR	
33.12	Lilliantite $\text{Pb}_3\text{Bi}_2\text{S}_8$ Polished	HR	
3411	Bournonite PbCuSbS_3 Cornwall, polished	85	low
344	Freislebenite $\text{Pb}_3\text{Ag}_5\text{Sb}_5\text{S}_{12}$ Polished	HR	

TABLE 2—Continued

	<i>Mineral</i>	e Thermoelectric power, ref. Cu microvolt/° C.	ρ Specific resistance Ohm. cm.
351	Boulangerite $Pb_6Sb_4S_{11}$ Stevens Mine, Wash. Deer Lodge, Mont. two samples	—135 —900 HR	med. high
354	Miargyrite $AgSbS_2$ Freiberg, polished Idaho	HR HR	
356	Matildite $AgBiS_2$ Cobalt, Ontario	—150	med.
3592	Emplectite $CuBiS_2$ Saxony, polished	HR	
35.11	Teallite $PbSnS_2$ Montserrat, Panza, Bolivia Bolivia, 2 samples	80 HR	high
3621	Cosalite $Pb_2Bi_2S_5$ Ontario, polished	—330	med.
363	Franckeite $Pb_5Sn_3Sb_2S_{14}$ With needle tin, Bolivia Bohemia	40 HR	420
365	Ramdohrite $Pb_3Ag_2Sb_6S_{13}$	HR	
367	Jamesonite $Pb_4FeSb_6S_{14}$ Idaho	HR	
388	Zinkenite $Pb_6Sb_{14}S_{27}$	HR	
38.10	Berthierite $FeSb_2S_4$ Braunsdorf, Saxony Braunsdorf, Saxony polished	450 310	med. med.
38.11	Cylindrite $Pb_3Sn_4Sb_2S_{14}$ Bolivia Bolivia	180 HR	high
391	Livingstonite $Hg_3Sb_4S_7$ Mexico, polished	HR	

TABLE 2—Continued

	<i>Mineral</i>	<i>e</i> Thermoelectric power, ref. Cu microvolt/° C.	<i>ρ</i> Specific resistance Ohm. cm.
4511	Rutile TiO ₂ Kragero, Norway var. nigrine, Arkansas	HR -540	high
4512	Pyrolusite MnO ₂ Lake Valley, New Mexico Polished	HR -165	electrolytic cond. electrolytic cond.
6112	Pyrochroite Mn(OH) ₂ Alum Rock, San Jose, Calif.	-400	high
625	Psilomelane BaMn ² Mn ⁴ ₈ O ₁₆ (OH) ₄ Woodstock, Va. Polished	-140 -150	10 ³ med.
7216	Magnetite FeFe ₂ O ₄ Clifton Mine, N. Y.	-53	low
7221	Hausmannite MnM ₂ O ₄ Långban, Sweden	HR	

the measurement of the temperature difference (Δt). The temperature of the hot junction was very nearly 100° C., while the cold junction was generally around 10° C. Copper was used as the reference metal, connecting the apparatus to a potentiometer. A double pole, double throw switch was used to connect the differential temperature measuring thermocouple, or the thermoelectric *EMF* to the potentiometer. Another similar switch was used as required for positive or negative thermoelectric power determinations. The thermoelectric power between 100° C. and the cold junction is the thermoelectric *EMF* and the thermoelectric power (*e*), expressed in microvolt/° C. is obtained as $e = EMF/\Delta t$.

Several measurements were made on each specimen and the thermoelectric power is given as the average of these measurements. Many specimens showed rather constant values, but some differed considerably, various spots on the same specimen showing considerable differences and even sign reversals. The thermoelectric power could be determined on rather small specimens, measuring about 1 to 2 mm. in length. If necessary, fragments of the mineral could be compressed into a small pellet and used for measurements. Such small fragments were not suitable for

the determination of the specific resistance and that is the reason that Table 2 summarizing the results, contains more data of thermoelectric power values.

Minerals of specific resistance in excess of $\rho = 10^6$ Ohm. cm (approximately) could not be measured accurately with the arrangement used and they are marked as *HR* ("high resistance") samples. In some cases the mineral sample was not available for cutting into prismatic shape and the specific resistance could not be measured, although it is indicated as medium resistance ($\rho =$ approximately 1 to 10^3) or low resistance (ρ less than 1 Ohm. cm).

The results of the measurements are summarized in Table 2 listed in the order given in Dana's System of Mineralogy by Palache, Berman and Frondel, vol. I, 1944. The species numbers adopted in the above work have been used.

3. DISCUSSION AND CONCLUSIONS

A certain correlation between the thermoelectric power and the resistivity is to be expected, because materials of high thermoelectric power generally are of higher resistivity. This correlation is not well established, because impurities may cause great variations in the resistivity without influencing the thermoelectric power (for instance galena, etc.).

The largest groups of minerals examined—the sulfides—are examined for a correlation of the measured electrical properties with the periodic table of the elements.

SULFIDES

GROUP I B (Cu, Ag, Au). *Chalcocite* Cu_2S always shows a rather high positive thermoelectric power, its resistivity being rather low. *Covellite* CuS , on the contrary has a very low negative thermoelectric power and very low resistivity. *Argentite* Ag_2S , has a very high negative thermoelectric power and a high resistivity.

GROUP II B (Zn, Cd, Hg). *Sphalerite* ZnS and *metacinnabar* HgS of positive thermoelectric power have a high resistivity, while *greenockite* CdS , *wurtzite* ZnS and *cinnabar* HgS are insulators.

GROUP IV A (Ge, Sn, Pb). A single sample of *germanite* [(Cu, Ge) (S, As)] had negative thermoelectric power, the large number of samples of *galena* PbS , were mostly negative, in the -200 to -450 microvolt/ $^\circ\text{C}$. range. There were a few positive samples of galena (argentiferous?) and occasionally positive and negative spots could be found on the same sample. The resistivity was very low, of the order of 0.01 Ohm. cm, but

occasionally much higher values were observed. No simple correlation could be found between the thermoelectric power and resistivity.

GROUP V A (As, Sb, Bi). In this group *realgar* AsS, *orpiment* As₂S₃, and *stibnite* Sb₂S₃ are insulators, while *bismuthinite* Bi₂S₃ shows a negative thermoelectric power with high resistivity.

GROUP VI B (Cr, Mo, W). *Molybdenite* MoS₂ samples show large positive or negative thermoelectric power values and occasionally spots of opposite sign occur on the same sample. The resistivity was of the order of 10 Ohm. cm. *Tungstenite* WS₂ is an insulator.

GROUP VII B (Mn, Ma, Re). Both *alabandite* MnS and *hauerite* MnS₂ are insulators.

GROUP VIII (Fe, Co, Ni, etc.), *Troilite* and *pyrrhotite* Fe_{1-x}S show variable low thermoelectric power values and low resistivity. *Pyrite* FeS₂ can be positive or negative, with great variations in the magnitude of the thermoelectric power and the resistivity. *Marcasite* FeS₂ is always positive. *Linnacite* Co₃S₄ in two samples showed variable thermoelectric power. *Millerite* NiS and *polydymite* Ni₃S₄ of rather low resistivity had a negative thermoelectric power of the same magnitude as that of pure Ni. *Pentlandite* (Fe, Ni)₉S₈ is of low thermoelectric power and low resistivity, while *violarite* Ni₂FeS₄ is negative and *bravoite* (Fe, Ni)₂S is positive.

Bornite Cu₅FeS₄ of positive thermoelectric power and rather low resistivity is similar to Cu₂S, while *chalcopyrite* CuFeS₂ of variable resistivity is always highly negative. *Cubanite* CuFe₂S₃ is less negative and of rather low resistivity, while *stannite* Cu₂FeSnS₄ is positive and of high resistivity.

COMPLEX SULFIDES

The minerals of this group are mostly combinations of the sulfides of Cu, Ag, Fe, Pb and Sn, with those of As, Sb, Bi. It is possible to note certain regularities in these combinations.

Cu₂S, which has a high positive thermoelectric power and rather low resistivity, in combination with As-sulfides retains its high positive value, although with an increase in resistivity (*tennantite*, *enargite*). In combination with the sulfides of Sb or Bi the high positive thermoelectric power remains unchanged, but the resistivity increases considerably.

Ag₂S of high negative thermoelectric power and high resistivity shows increased resistivity and variable changes in the thermoelectric power.

Galena, PbS, generally shows increased resistivity with negative thermoelectric power predominating, when in combination with other sulfides.

ARSENIDES

The thermoelectric powers of the arsenides of Cu, Ag, Fe, Co, Ni are

invariably negative. The resistivity could not be measured exactly, but the quantitative indications show a low resistivity. The sulfoarsenide *arsenopyrite* FeAsS has a considerably higher negative thermoelectric power than the comparable arsenide FeAs_2 (*löllingite*). Its resistivity is variable but not high. The other sulfoarsenides show intermediate thermoelectric power values between the corresponding arsenides and sulfides.

OTHER MINERALS

The relatively few tellurides show low negative thermoelectric power values and their resistivity is not high. The oxides of Ti, Mn and Fe are of high negative thermoelectric power and high resistivity.

CONCLUSIONS

The thermoelectric power and the resistivity of the observed minerals indicate that definite order of magnitude values can be established. Variations between different samples of the same mineral are probably due to impurities.

Correlation with the periodic system appears to indicate—in the sulfide group—that low resistivity occurs only in the first horizontal column of group I *B* (Cu) and group VIII (Fe, Co, Ni) and in the third horizontal column of group IV *A* (Pb) and V *A* (Bi). The second horizontal column of group VI *B* (Mo) and I *B* (Ag) show intermediate resistivity.

The thermoelectric power is correlated with the valence and the crystal forms in group I *B* (Cu) and VIII (Fe).

The data obtained should be helpful in the study of semiconductors and in the understanding of the electric properties of these materials.

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