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ELECTRICAL RESISTIVITIES AND TEMPERATURE COEFFICIENTS OF LEAD, TIN, ZINC AND BISMUTH IN THE SOLID AND LIQUID STATES

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Abstract

A method of measuring the resistance-temperature coefficients of low melting point metals in the solid and liquid states is described. Previous difficulties in the way of making such measurements have been largely eliminated by employing oxide films as containers for the molten metals. The resistivity-temperature curves are shown for the metals (Pb, Sn, Zn, Bi), and the resistance-temperature coefficients are given for 20° intervals throughout the range 20° to 460°C. The temperature coefficients of resistance of zinc above the melting point are found to be positive instead of negative as reported by Northrup and Suydam. Variations in the resistivity values indicate that there are allotropic transformations in zinc slightly above 180°C and at about 340°C. The coefficients of the metals investigated are all positive except those for nonannealed bismuth in the regions 160° to 180°C and 225° to 275°C and those for annealed bismuth in the latter region. The high resistivity values of nonannealed bismuth below 160°C are attributed to three possible factors, (a) lack of random orientation of the crystals, (b) cracks and imperfections in the crystal lattice, and (c) amorphous solid bismuth which may be formed between cleavage faces and in reentrant angles. The origin of these factors is accounted for by a crystalline transformation, in the region 160° to 180°C, which gives rise to them only when the metal is cooled rapidly. When nonannealed bismuth passes through this region from the lower to the higher temperature the negative coefficients are then to be expected. In the range 225° to 275°C the negative coefficients of bismuth are due to a molecular derangement of the metal as it approaches the melting point and passes from the solid to the liquid state.

IN A previous paper "Liquid Wires and their Surface Films"[1] the authors reported a study of the functions of oxide films in supporting molten wires of lead, tin, zinc and bismuth. Reference was made to a method of measuring the resistance-temperature coefficients of low melting point metals in the solid and liquid states. The object of the present article is to describe this method and to give the electrical resistivity and temperature coefficients of lead, tin, zinc and bismuth in the temperature range 20°C to 460°C.

Experimental Procedure

The lead, tin, zinc and bismuth wires were mounted and heated in a nitrogen container. The container was a brass cylinder, 18 cm in length and 9 cm in diameter, with one end removable. The method of support of the wires in the container is given in Fig. 1. Brass blocks, $B\,B'$, each of 2 cc volume, were mounted firmly, 5.25 cm apart, with their upper faces flush with P, the horizontal porcelain plane of support for the wires. Holes, $s\,s'$, 0.9 mm in

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[1] Pietenpol and Miley, Phys. Rev. [2] **30**, 697–704 (1927).

diameter were drilled in the upper part of the blocks near the inner edge and coated on the inside with Wood's metal so that good contact was made with the clean ends of the wires. (The melting point of the Wood's metal could not be detected in any of the readings.) The holes extended 5 mm into the blocks, and for the lead, tin, and zinc wires they were inclined at a 30° depression angle to the horizontal. They were horizontal for the bismuth wire which would not permit bending. There were four copper wires, No. 8 A.w.g., leading through the center of tubes, in the removable end of the container. The tubes were filled with asbestos cement of high insulating quality. Two of these copper wires were brazed to each of the brass blocks; one pair of them, 1-2 in Fig. 1, was used to conduct a small current through the wire *W* under investigation, and the other pair, 3-4, served in the measurement of the potential drop. The entire support for the lead, tin, zinc and bismuth wires could be removed from the container for changing the wires.

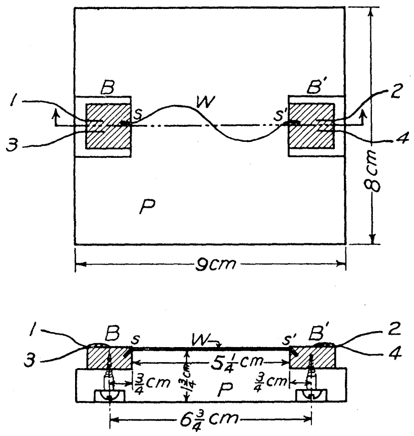

Fig. 1. Diagram showing method of support of wires.

After a wire was suspended between the brass blocks, it was heated by sending an electric current through it while in air in order to strengthen the oxide film. The vessel containing the suspended wire was then filled with nitrogen and placed in an electric furnace. The inlet and outlet tubes for nitrogen were closed with porous asbestos plugs which permitted the gas to remain constantly at atmospheric pressure. The temperature of the furnace was measured by a nickel-chromium thermocouple, which was inserted into the container through an asbestos filled tube, so that it registered the temperature in the vicinity of the wire being investigated.

The thermal e.m.f. and the potential drop across the suspended wire were measured by means of potentiometers. A single potentiometer was used to control the current through the heated wire and to measure the potential drop across the wire in order to make the manipulation more convenient. The current was 1/100 of the magnitude of the e.m.f. of the standard cell since the standard resistance used was 100 ohms. The current through the heated wire was 10.19 milliamperes and was kept constant to within 1/100 of a milliampere. The resistance with the current in both directions was determined in order to eliminate thermal e.m.f. which were found to be very small.

MATERIALS

The lead and tin wires were 14.764 cm in length and 0.75 mm in diameter. The dimensions of the zinc wire were 14.923 cm in length and 0.75 mm in diameter. The nonannealed bismuth wire was 5.239 cm in length and 0.74 mm in diameter, and the annealed bismuth wire was 5.412 cm in length and 0.81 mm in diameter. The wires used were obtained from Baker and Company, Inc., and their chemical analyses were as follows:

C. P. Lead—Gold, arsenic, antimony, copper = minute traces; no bismuth.
C. P. Tin — Lead = 0.007% iron = 0.002%
copper = 0.003 arsenic and sulphur,
tin = 99.988 traces each.
C. P. Zinc —Iron = 0.005% cadmium = 0.0018%
lead = 0.0004 arsenic and sulphur,
zinc = 99.993 traces each.
C. P. Bismuth—Better than 99.9% bismuth.

RELIABILITY OF THE METHOD

To one unfamiliar with the ability of an oxide coat to retain the shape of a molten metal, the reliability of the method may seem open to question. Careful experiments were made in passing from the liquid to the solid and back to the liquid state, which convinced the authors that the oxide film was dependable as a container. For example, the resistivity of liquid bismuth at the melting point was found to be 124.070 microhm-cm. It was then solidified and brought back to the melting point when its resistivity was 124.192 microhm-cm. In the case of tin, readings were taken on increasing and decreasing temperatures for two samples of different lengths cut from the same wire. Both samples were twice taken from room temperature to the melting point and back. The resistivities of the first sample as measured in the liquid state at the melting point were 47.22 and 47.25 microhm-cm. For the second sample the values were 47.25 and 47.20 microhm-cm. These values check to approximately 0.1 percent which is well within the experimental error.

Fig. 2 shows curves for tin on increasing and decreasing temperatures in the neighborhood of the melting point. The curve *AB* is for increasing temperature after the wire had been previously liquefied and slowly cooled to room temperature. The rounding of the curve preceding the melting point would indicate a gradual change in structure which has not been emphasized by previous experimenters. That this is not due to possible impurities in the metal seems evident from the fact that the point *B* at which the slope of the curve suddenly changes, checks, within the degree of accuracy of the experiments, exactly the melting point of tin, 231.9°C. This was true in the case of tin for all four of the determinations mentioned above, and in the case of all other metals the agreement was very close.

With decreasing temperature, the curve of Fig. 2 falls slightly from *B* to *C* indicating a supercooling of the metal. The point *C* was carefully determined and found in this case to be slightly above 223°C. In several determinations made on tin the average value for the supercooling was 9°C. A similar supercooling was found for bismuth, but no tests were made for lead and zinc. With decrease in temperature below the point *C*, the curve falls rapidly but not suddenly to meet the curve *AB*. This "setting" of a metal is a phenomenon of common observation though its effect upon resistivity has hitherto apparently not been mentioned. As yet no careful observations have been made upon this lag in change of resistivity with different rates of cooling. The readings plotted in Fig. 2 were made with the furnace cooling at the rate of approximately six degrees per hour.

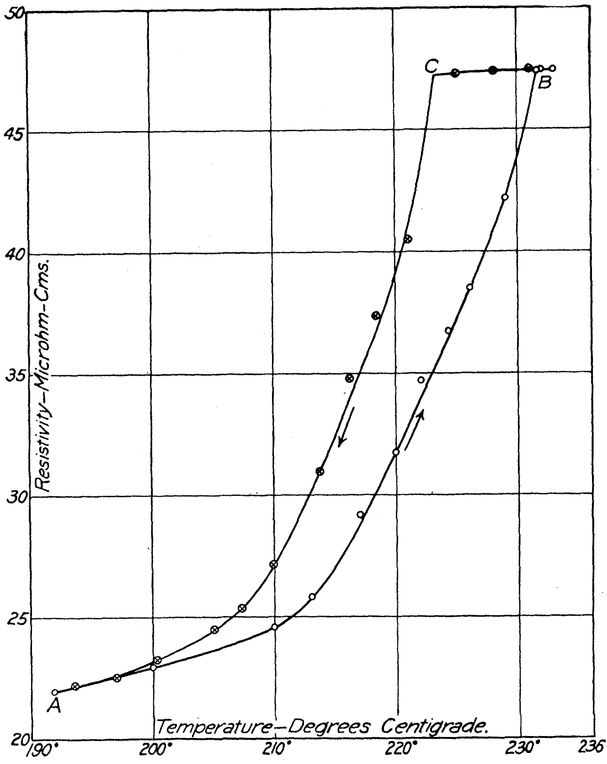

Fig. 2. Resistivity-temperature curves for tin in melting point region.

In order to use an oxide film as a container in measuring resistivities of metals through the solid and liquid states, it is necessary that a good film be formed and that the temperature be changed very slowly in passing from one state to the other. In the liquid state the metal must not be disturbed, and because of the supercooling referred to above the method is better adapted to readings made with increasing than with decreasing temperatures. Further, with decreasing temperatures a non-oxidizing gas must be constantly forced into the furnace with danger of disturbing the temperature equilibrium. The data which follow have in all cases been taken with increasing temperatures.

CORRECTIONS

Corrections were made in the resistivities of the metals for the expansions of the metals as the temperature was increased. Below the melting points the radial and longitudinal expansions of the wires are the same per unit of length. From a consideration of the volume coefficients of expansion of the metals it is found that for each 20°C interval the resistivities obtained below the melting points should be increased by the following amounts: lead, 0.058%; tin, 0.054%; zinc, 0.060%; and bismuth, 0.027%.

The dimensions of the brass blocks and that of the porcelain supporting plane were such, between the points of contact, as to neutralize one another's effects on the length of the bismuth wires as the temperature was increased. This factor was not considered in the case of the other three wires since they were bent in the shape of an *S* and were not affected by such a factor. Because of the close checks on resistivities indicated in the previous section it seems logical to assume that the oxide film acts as an elastic membrane. Thus when the volume changes in passing through the melting point and above the melting point, corrections are made assuming that the films are isotropic and therefore that the radial expansion is twice the longitudinal expansion per unit of length. For an elastic membrane this is apparent from a consideration of Fig. 3. If a membrane in the form of a right circular cylinder of radius r and length L is under a tension due to an internal pressure, p, in the liquid which it contains, the force on the section *abcd*, when in equilibrium, is $2rLp=2T_1L$ from which the tension, T_1, in the film per unit length, tangent to the circumference of the circular cylinder, is $T_1=rp$. Also the force on the circular section, *efgh*, is $\pi r^2 p=2\pi r T_2$ from which the tension, T_2, in the film per unit length, in the longitudinal direction, is $T_2=rp/2$. Thus since the change in T_1 is twice as great as that in T_2 for a given increment in p it follows as stated above that the radial and longitudinal strains are in the same ratio.

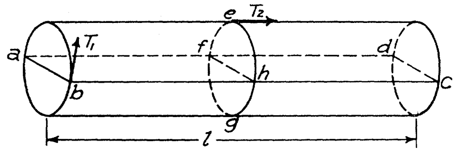

Fig. 3.

Considering the expansion of lead[2] 0.0348 cc per cc, the expansion of tin[2] 0.0310 cc per cc, the contraction of bismuth[2] 0.0330 cc per cc, and the ex-

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[2] G. Vicentini and D. Omodei, Atti. Acad. Torino **23,** 38 (1888).

pansion of zinc[3] 0.0692 cc per cc, the following corrections were made in the resistivities above the melting points due to the change in volumes in passing through the melting points: lead, an increase of 2.075%; tin, an increase of 1.852%; bismuth, a decrease of 1.925%; and zinc, an increase of 4.129%. Taking for each 20°C interval the expansion of molten lead[2] 0.00232 cc per cc, the expansion of molten tin[4] 0.00197 cc per cc, the expansion of molten bismuth[5] 0.00240 cc per cc, and the expansion of molten zinc[6] 0.00176 cc per cc, the following corrections were made for each 20°C interval above the melting points due to the change in volume in passing through the interval: lead, 0.139% increase; tin, 0.118%; bismuth 0.114%; and zinc, 0.106%.

The electrical resistivity of the oxides of these metals as given by Friedrich[7], Sommerville[8] and Horton[9] is more than 10^{10} times the resistivity of the metals. Thus the resistivity correction for the metallic oxide film is negligible in every case. The thickness of the oxide film is such that it falls within the limits of the experimental error in the measurement of the diameter of the wire. These are distinct advantages of the oxide film method of measuring the resistivity of low melting point metals in the liquid state.

DEFINITION OF RESISTANCE-TEMPERATURE COEFFICIENT

Various definitions are in use for the resistance-temperature coefficients of metals. The formula which has been much used for expressing the relation between resistance and temperature is:

$$R = R_1(1 + a_1(t - t_1)) \tag{1}$$

in which R_1 is the resistance at the reference temperature t_1, R is the resistance at any temperature t, and a_1 is the temperature coefficient of resistance for the reference temperature t_1. The value of a_1 at the temperature t_1 depends upon R_1, and when the slope of the resistivity-temperature curve is not constant it is also dependent upon the temperature interval $t - t_1$.

The most exact definition of the "temperature coefficient at t_1", a_{t1}, is given by the equation:

$$a_{t_1} = (dR/Rdt)_{t_1}. \tag{2}$$

This equation applies to any variation of resistivity with temperature.

The temperature coefficients of resistance given in the present work are defined by the equation:

$$a_{t_1,t_2} = \frac{2(R_2 - R_1)}{(R_2 + R_1)(t_2 - t_1)} \tag{3}$$

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[3] M. Toepler, Wied. Ann. **53**, 343 (1894).

[4] A. L. Day, R. B. Sosman, and J. C. Hostetter, Amer. Journ. Sci. [4] **37**, 1 (1914).

[5] E. F. Northrup, Trans. Amer. Electrochem. Soc. **25**, 338 (1914).

[6] P. Pascal and J. Jouniaux, Comptes Rendus **158**, 414 (1914).

[7] E. Friedrich, Zeits. f. Physik **31**, 813 (1925).

[8] A. A. Sommerville, Met. Chem. Eng. **10**, 422 (1912).

[9] F. Horton, Phil. Mag. [6] **11**, 505 (1906).

[10] L. Holborn, Ann. d. Physik **59**, 146 (1919).

in which R_2 and R_1 are the resistivities respectively at t_2 and at t_1, and a_{t_1,t_2} is the temperature coefficient of resistance for the temperature interval t_1 to t_2. This is considered to be a satisfactory approximation of Eq. (2), for 20° intervals in the present work.

DISCUSSION OF THE RESULTS

The curves of Fig. 4 are reduced copies of the originals which were drawn on mm cross-section paper, 50×70 cm. This made it possible to read the resistivities to the fourth decimal place and the temperatures to the second decimal place. The resistivity-temperature relations were plotted and from the resulting curves the resistivities were read at the temperatures given in the Tables I-IV inclusive. From these resistivity values the temperature coefficients of resistance were calculated for the temperature intervals given in the tables by using Eq. (3). The measurements made on the metals represented in Fig. 4 were extended to above 600°C in most cases, but there was usually a noticeable deviation from a straight line beginning near 500°C. The upper temperature limit was arbitrarily taken as 460°C for each metal in the present work, and this is well within the dependable temperature range for these oxide containers.

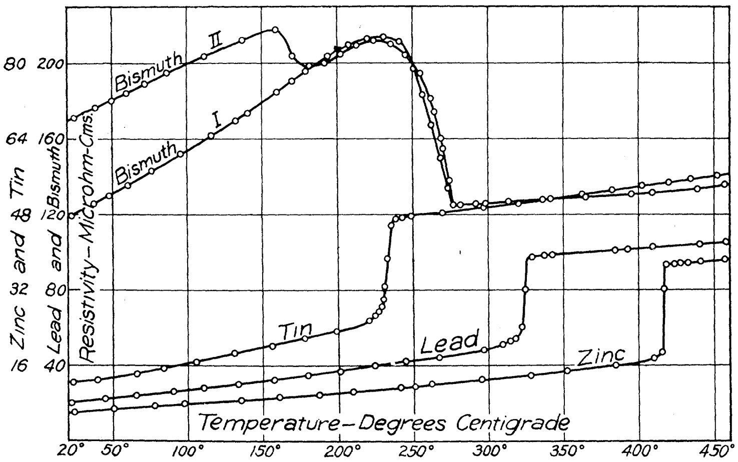

Fig. 4. Resistivity-temperature curves for lead, tin, zinc and bismuth.

The temperature coefficients of resistance possess a higher degree of accuracy than the resistivity values, for they are affected less by any experimental error that might be made in taking the volume measurements of the wires. However, since the wire-lengths were well marked, and the dimensions of the wires were carefully measured, there was little chance for the introduction of an error of appreciable magnitude. The resistance measurements were accurate to within 0.001 percent and the precision of reading the temperature was 0.01°C. The time interval during which the readings for the curves were taken varied from six to nine hours. Several series of readings were made upon different samples of a single metal which showed that the curves were reproducible to within a fraction of a percent, except for bismuth in the solid state where the variation was somewhat greater. The curves and tables are commented on separately for the different metals.

Lead. The curve for lead is slightly convex in the direction of the temperature axis for the solid state, and is a straight line for the liquid state. Table I shows a very good agreement in general with the values of resistivity as given by other experimenters at certain temperatures. The variation in the resistivity values of lead in the solid state is very regular and there is no indication of an allotropic transformation in the metal.

TABLE I. *Resistance-temperature coefficients and resistivity of lead.*

Temp. Range	a	Temp.	Resistivity microhm-cms	Other observers Resistivity	Authority
20°– 40°C	0.00336	20°C	20.648	22	(1)
				20.4 at 0°	(2)
40°– 60°	.00341	40°	22.084		
60°– 80°	.00335	60°	23.645		
80°–100°	.00332	80°	25.285		
				27.97 at 90.35°	(2)
100°–120°	.00311	100°	27.021	27.8	(3)
120°–140°	.00302	120°	28.787		
140°–160°	.00299	140°	30.582		
				32.79 at 142.7°	(2)
160°–180°	.00293	160°	32.468		
180°–200°	.00291	180°	34.413		
				36.90 at 196.1°	(2)
200°–220°	.00275	200°	36.478	38.0	(3)
220°–240°	.00273	220°	38.542		
240°–260°	.00251	240°	40.697		
260°–280°	.00246	260°	42.791		
280°–300°	.00322	280°	44.946		
300°–320°	.00665	300°	47.938		
320°–330°	.0554	320°	54.761	50.00 at 319°	(3)
330°–340°	.00116	330°	96.735	95.00 at 333°	(3)
340°–360°	.000576	340°	97.867		
360°–380°	.000570	360°	99.000		
380°–400°	.000577	380°	100.255		
400°–420°	.000561	400°	101.418	98.30	(3)
420°–440°	.000559	420°	102.563		
440°–460°	.000558	440°	103.716	100.55 at 450°	(3)
		460°	104.878		

(1) Bureau of Standards, Cir. No. 74, 317 (1918).
(2) J. Dewar and J. A. Fleming, Phil. Mag. **36,** 271 (1893).
(3) E. F. Northrup and V. A. Suydam, Journ. Frank. Inst. **175,** 153 (1913).

In order to compare the resistivity-temperature coefficients of lead with those previously given, the value 19.215 microhm-cm was obtained for the resistivity of lead at 0°C by extrapolation. Substituting these values for R_1 and t_1 and the values 27.021 microhm-cm and 100°C for R and t respectively in Eq. (1), the value $a_{0.100} = 0.00406$ was obtained for lead. The values of $a_{0.100}$ for several observers as given by Holborn,[10] vary from 0.00406 to 0.00422.

Tin. The curve for tin is a straight line for the liquid state but deviates from it slightly in the solid state. Table II shows that the value of the resistivity at 20°C is between Dewar and Fleming's value and that given by the Bureau of Standards. Dewar and Fleming's values are higher than the

TABLE II. *Resistance-temperature coefficients and resistivity of tin.*

Temp. Range	a	Temp.	Resistivity microhm-cms	Other observers	
				Resistivity	Authority
20°– 40°C	0.00365	20°C	12.853	11.50	(1)
40°– 60°	.00355	40°	13.828	14.14 at 18.75°	(2)
60°– 80°	.00325	60°	14.845		
80°–100°	.00309	80°	15.843	18.30 at 91.45°	(2)
100°–120°	.00293	100°	16.842		
120°–140°	.00278	120°	17.860		
140°–160°	.00273	140°	18.880		
160°–180°	.00328	160°	19.940	23.63 at 176°	(2)
180°–200°	.00395	180°	21.296		
200°–220°	.0178	200°	23.046	20.30	(3)
220°–232°	.0336	220°	31.822		
232°–240°	.000787	232°	47.250	47.60 at 235°	(3)
240°–260°	.000783	240°	47.580		
260°–280°	.000831	260°	48.331		
280°–300°	.000827	280°	49.142		
300°–320°	.000815	300°	49.961	49.44	(3)
320°–340°	.000804	320°	50.782		
340°–360°	.000795	340°	51.506	50.76 at 350°	(3)
360°–380°	.000780	360°	52.331		
380°–400°	.000771	380°	53.154		
400°–420°	.000760	400°	53.980	52.00	(3)
420°–440°	.000748	420°	54.807		
440°–460°	.000736	440°	55.633	53.30 at 450°	(3)
		460°	56.458		

(1) Bureau of Standards, Cir. No. 74, 317 (1918).
(2) J. Dewar and J. A. Fleming, Phil. Mag. **36**, 271 (1893).
(3) E. F. Northrup and V. A. Suydam, J. Franklin Inst. **175**, 153 (1913).

present values and in most cases Northrup and Suydam's are a little less. The variations in the resistivity values of tin are not interpreted as indicating any allotropic transformations in tin between 20° and 220°C. The value $a_{0.100} = 0.00418$ was obtained from Eq. (1) by considering the resistivity of tin at 0°C to be 11.878 microhm-cm. Some values that have been given[10] range from 0.0044 to 0.0047.

Zinc. The resistivity-temperature curve for zinc is probably a straight line for the liquid state. The agreement of the resistivities below the melting point with those of other experimenters is good. The value at 415°C is higher than Northrup and Suydam's value at the same temperature, due to the fact that their curve obtained with falling temperature breaks more sharply in this region. At 427°C which is just beyond the melting point their resistivity value, 37.30 microhm-cm agrees well with the value 37.142 microhm-cm, obtained in the present work. Beyond this point their resistivity values decrease for higher temperatures which is just opposite to the results obtained by the writers, as shown in Table III. As Northrup has stated,[11] the negative coefficients of zinc in the molten state have formed a stumbling block in all proposed theories of metallic conduction, and we believe from the present investigation that this difficulty has been removed.

The temperature coefficients of resistance of zinc in the solid state reach a minimum value between 160° and 180°C and between 320° and 340°C. From

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[11] E. F. Northrup, Journ. Frank. Inst. **179**, 640 (1915).

TABLE III. *Resistance-temperature coefficients and resistivity of zinc.*

Temp. Range	*a*	Temp.	Resistivity microhm-cms	Other observers Resistivity	Authority
20°– 40°C	0.00385	20°C	5.921	5.8	(1)
40°– 60°	.00355	40°	6.395	6.2 at 18.8°	(2)
60°– 80°	.00333	60°	6.868		
80°–100°	.00312	80°	7.343	7.91 at 92.45°	(2)
100°–120°	.00294	100°	7.816	7.95	(3)
120°–140°	.00277	120°	8.289		
140°–160°	.00247	140°	8.763		
160°–180°	.00221	160°	9.207		
180°–200°	.00255	180°	9.622	10.37 at 191.5°	(2)
200°–220°	.00270	200°	10.125		
220°–240°	.00283	220°	10.687		
240°–260°	.00268	240°	11.309		
260°–280°	.00242	260°	11.931		
280°–300°	.00204	280°	12.523		
300°–320°	.00191	300°	13.045	13.25	(3)
320°–340°	.00183	320°	13.559		
340°–360°	.00206	340°	14.062		
360°–380°	.00253	360°	14.655		
380°–400°	.00458	380°	15.417		
400°–410°	.00500	400°	16.897		
410°–415°	.00533	410°	17.763		
415°–423°	.0845	415°	18.243	17.00	(3)
423°–440°	.000625	423°	36.955	37.30 at 427°	(3)
440°–460°	.000576	440°	37.349	37.20	(4)
		460°	37.783	37.08 at 450°	(3)

(1) Bureau of Standards, Cir. No. 74, 317 (1918).
(2) J. Dewar and J. A. Fleming, Phil. Mag. **36,** 271 (1893).
(3) E. F. Northrup and V. A. Suydam, J. Franklin Inst. **175,** 153 (1913).
(4) L. de la Rive, Comptes Rendus **57,** 698 (1863).

this it may be inferred that there are allotropic transformations in zinc near these regions of minima. By plotting the resistivity values of zinc given in Table III from 20° to 400°C on mm cross-section paper, 60×80 cm, the breaks in the curve become pronounced between 180° and 200°C and between 320° and 360°C. The change is so gradual that no point can be designated with certainty as the point of transition. The data of different resistivity curves show that the greatest changes probably occur at slightly above 180°C and at about 340°C.

The irregularities in the variation of certain properties of zinc with the temperature have led a number of investigators to suspect one or more allotropic transformations of zinc. Le Chatelier[12] found a transition point in zinc between 340° and 350°C from electrical resistance measurements; and Benedicks[13] found two slight breaks in the temperature-resistance curve (a) between 160° and 170°C, and (b) between 320° and 330°C. Monckmeyer[14] and Werner[15] confirmed Le Chatelier's point which has been identified with Benedick's second point. Miss Bingham's work[16] on the electrical resistance of zinc shows a critical point between 200° and 210°C, and between 330° and

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[12] H. le Chatelier, Comptes Rend. **3,** 414, 454 (1890).

[13] C. Benedicks, Arkiv. Matem. Astron. Fysik **6,** 24 (1910).

[14] K. Monckmeyer, Zeits. f. anorg. Chem. **43,** 182 (1905).

[15] M. Werner, Zeits. f. anorg. Chem. **83,** 275 (1913).

[16] K. E. Bingham, Journ. Inst. Metals **24,** 333 (1920).

340°C. From her measurements on electrical conductivity, electrolytic potential, density, hardness, and mechanical properties of the metal it is suggested that zinc has three allotropic modifications and that the transition temperatures are about 180°C and 310°C. Pierce, Anderson and Van Dyck[17] conclude, from x-ray diffraction patterns, that within the limits of experimental error, there are no allotropic transformations in zinc in the temperature range 20° to 400°C. The e.m.f. temperature curves of Stockdale,[18] obtained by using electrodes of pure zinc in a special electrolyte, indicate that zinc undergoes a transformation at about 315°C. From a consideration of the existing experimental evidence it seems safe to conclude that there are two allotropic transformations in zinc (a) between 170° and 200°C, and (b) between 310° and 350°C.

The value 5.446 microhm-cm was obtained for the resistivity of zinc at 0°C by extrapolation, and by substituting in Eq. (1) as was done for lead, the value $a_{0.100}=0.00435$ was obtained for the coefficient of zinc. Holborn[10] gives the values of several observers for $a_{0.100}$for zinc which vary from 0.00402 to 0.00417.

Bismuth I. The wire used in obtaining the curve for bismuth I Fig. 4 was well annealed and a microscopic study of the cross-section showed that all crystal orientations* were present. The general outline of this curve agrees well with the one given by Northrup and Suydam with falling temperature and possibly a random crystal orientation. It also agrees well in form with the ones given by Kapitza[19] with falling temperature and with the resistivity measurements made perpendicular or parallel to the cleavage planes. The greatest difference is that their curves break more suddenly at the melting point and have a higher and sharper peak for the solid state near the melting point. Kapitza mentions that some of his curves showed flatter peaks than the ones that he gave. The agreement is very good between the resistivity values given in Table IV and those that have been given by previous experimenters with the exception of the peak values referred to above.

By taking 110.313 microhm-cm for the resistivity of bismuth I at 0°C and substituting in Eq. (1) the value $a_{0.100}=0.00401$ was obtained. The values of some other observers[10] vary from 0.00438 to 0.00458. By taking 112.0 microhm-cm as Northrup and Suydam's value of the resistivity of bismuth at 0°C the value $a_{0.100}=$ 0.00397 was found. Thus it appears that there is considerable variance in the values of $a_{0.100}$ given by the work of different investigators. The agreement between the value of $a_{0.100}$ given by Northrup and Suydam's work and the one obtained in the present work is well within the limits of the accuracy of the extrapolation.

Bismuth II. The curve for bismuth II in Fig. 4 is representative of those that have been obtained in this laboratory with samples of nonannealed bis-

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[17] W. M. Pierce, E. A. Anderson and P. Van Dyck, Journ. Frank. Inst. **200,** 349 (1925).

[18] D. Stockdale, Journ. Chem. Soc. **127,** 2951 (1925).

[19] P. Kapitza, Proc. Roy. Soc. **A119,** 358 (1928).

* The angle between the trigonal axis of the crystal and the length of the wire is defined as the orientation.

TABLE IV. *Resistance-temperature coefficients and resistivity of bismuth.*

			Resistivity	Other observers	
Temp. Range	a	Temp.	microhm-cms	Resistivity	Authority
20°– 40°C	0.00311	20°C	119.323	120.00	(1)
40°– 60°	.00320	40°	126.979	120.00 at 17.5°	(2)
60°– 80°	.00337	60°	135.382	119.00 at 18°	(3)
80°–100°	.00328	80°	144.719		
100°–120°	.00293	100°	154.523	156.50	(2)
120°–140°	.00277	120°	163.859	160.20 at 100°	(3)
140°–160°	.00321	140°	173.196	181.65 at 150°	(2)
160°–180°	.00299	160°	184.866		
180°–200°	.00246	180°	196.257		
200°–220°	.00164	200°	206.154	214.50	(2)
220°–230°	.000434	220°	212.877		
230°–240°	−.000972	230°	213.800		
240°–260°	−.01019	240°	211.943		
260°–278°	−.01806	260°	172.729		
278°–300°	.000322	278°	124.430		
300°–320°	.000384	300°	125.316	128.90	(2)
320°–340°	.000405	320°	126.282		
340°–360°	.000417	340°	127.310	131.55 at 350°	(2)
360°–380°	.000431	360°	128.376		
380°–400°	.000467	380°	129.486		
400°–420°	.000491	400°	130.711	134.20	(2)
420°–440°	.000570	420°	132.000		
440°–460°	.000637	440°	133.513	137.00 at 450°	(2)
		460°	135.224		

(1) Bureau of Standards, Cir. No. 74, 317 (1918).
(2) E. F. Northrup and V. A. Suydam, J. Franklin Inst. **175,** 153 (1913).
(3) W. Jaeger and H. Diesselhorst, Wiss. Abh. d. Phys. Techn. Reichsanstalt **3,** 269 (1900).

muth. The bismuth II wires were very brittle and would not permit bending while the bismuth I wires were flexible enough to be wound into a spiral. The variation of the resistivity values of the two types of wires was less than one percent in the liquid state. The bismuth referred to by the authors[20] in a previous report was of the type of bismuth II. A study of the discrepancies between the values obtained for the resistivity of bismuth II in the solid state and the values given by other experimenters led to curves of the type of bismuth I which, as already stated, agree well with those given by previous investigators. The wire used for obtaining the curve for bismuth II was drawn by Baker and Company, Inc., and nonannealed wires that were drawn in this laboratory showed similar electrical properties. A microscopic study of the cross-section of bismuth II showed that the crystal orientation was about 0° in the center of the wire and became more and more random towards the circumference of the cross-section. From this one would expect bismuth II to have a higher resistivity than bismuth I in the solid state. It is well known that the resistivity of bismuth is greater along the trigonal axis than across it.

The explanation of the variation of the resistivity of bismuth, when measured in different directions, as due to fissures or cracks between cleavage planes perpendicular to the trigonal axis has come to be pretty generally accepted. Borelius and Lindh[21] seem to believe that most, if not all, of the differences observed between the resistivities of bismuth in different directions

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[20] Pietenpol and Miley, Phys. Rev. [2] **33,** 294 (1929).

[21] G. Borelius and A. E. Lindh, Ann. d. Physik **51,** 607 (1916); and **53,** 124 (1917).

are due to fissures and internal stresses. Bridgman[22] attributed the high resistivity observed by different experimenters perpendicular to the cleavage plane to the existence of fissures parallel to the main cleavage plane. Schneider,[23] who finds a high ratio between the resistivities measured perpendicular and parallel to the main cleavage plane, apparently accepts Bridgman's explanation. The high resistivity values recently observed by Bridgman,[24] for specimens in which the bending was known to be severe, are accounted for by means of fissures. Kapitza's reduction of the abnormally high resistivity of some specimens by compression may be referred to as good evidence of the existence of fissures between the cleavage planes. The resistivity values of bismuth measured perpendicular to the main cleavage plane vary from 138 microhm-cm, Bridgman's value when precautions are taken to avoid fissures, to 206 microhm-cm. Kapitza has explained the variation in the resistivity values at a given orientation as due to minute cracks and imperfections in the crystal lattice. The hypothesis suggested to account for the origin of the cracks is a crystalline transformation slightly below the melting point, which gives rise to the cracks during the change of shape that accompanies the transition. Kapitza mentions that the suggestion has been made that the transformation is possibly from the rhombohedral class of the hexagonal system to some class of the cubic system. The present investigation indicates that the region of this allotropic transformation is 160° to 180° C. The experimentally determined point on the curve of bismuth II that is nearest the beginning of this region of negative coefficients is 160.78°C. A transition temperature has been designated as 75°C,[25] 112° and 161°C.[26]

We now believe that there are three factors that contribute to the high resistivity values for bismuth II in the temperature range 20° to 160°C, (a) the crystal orientation referred to above, which approached 0° at the center of the wire, (b) the cracks and imperfections in the crystal lattice which result from rapid cooling of the wire through the region of the allotropic transformation, and (c) the presence of amorphous solid bismuth of abnormal resistivity which may be formed between the contact faces and in the re-entrant angles in addition to the cracks. The fact that the resistivity values of bismuth I and bismuth II are nearly the same for temperatures above 180°C indicates that the factors contributing the high values for bismuth II below 160°C are largely eliminated in passing through the range 160° to 180°C. This is good evidence of an allotropic transformation. Otherwise it would be hard to account for the removal of factor (a) which was observed to be present in bismuth II and not in bismuth I. No break was detected in the curves of bismuth I in passing through the region of the transition. This might be considered as favoring the suggestion that the transformation is from the rhombohedral to some cubical form since such a transition would not be expected to result in a very great change in resistivity.

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[22] P. W. Bridgman, Proc. Amer. Acad. Arts and Sci. **60,** 361 (1925).

[23] G. W. Schneider, Phys. Rev. [2] **31,** 251 (1928).

[24] P. W. Bridgman, Proc. Amer. Acad. Arts and Sci. **63,** 351 (1929).

[25] E. Cohen and A. Moesveld, Zeits. f. Phys. Chem. **85,** 419 (1913).

[26] E. Janecke, Zeits. f. Phys. Chem. **90,** 313 (1915).