Study on the Transformation of Zinc by Electric Resistance in Connection with Eutectic Phenomena

Study on the Transformation of Zinc by Electric Resistance in Connection with Eutectic Phenomena*

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Synopsis

Accurate measurements of the electric resistance of zinc were made by the potentiometer method in the range of temperature from room temperature up to 350°C. The anomalous changes were observed at the temperatures, 170, 200, 230 and 320°C. The first two temperatures were explained respectively to be the eutectic temperatures of the solders, Pt-Sn-Zn and Sn-Zn systems, used to solder the potential lead and the specimen; 230°C to be the temperature of second separation in the former solder; 320°C to be the eutectic temperature of the alloy, Pd-Zn system formed in the specimen. From a conception explaining the eutectic phenomenon, 170°, 200° and 320°C were considered to be anomalies of zinc itself.

I. Introduction

Many workers have studied the anomalous changes of the electric resistance of zinc at high temperatures. Le Chatelier[1] observed a bend at 360°C in the resistance-temperature curve. Benedicks[2] observed, together with this change at 330°C, another one at 170°C, and inferred that zinc had three allotropies. Werner[3] observed a breaking at 340°C but none in the neighborhood of 170°C. Benedicks and Arpi[4] made preciser measurements with a specimen, 99.991 per cent pure, and with one containing impurities, such as cadmium, with the results that an anomaly was not observable in the former, while it appeared in the latter. Accordingly, they concluded that zinc had no transformation, and that the anomalous change formerly observed was the effect of the impurity. Holborn[5] studied temperature coefficients of the electric resistance of various metals and pointed out that only the resistance of zinc showed a slight deviation from a linear change. K. E. Bingham[6] found two gaps at 200 and 330°C. Pietenpol and Miley[7] determined the resistivity of highly pure zinc (99.993 per cent) at high temperatures and observed two loose breakings in the neighborhoods of 180 and 320°C. Grube and Burkhardt[8] constructed a phase diagram of Cd-Zn system from their studies of the resistance of these alloys, and found no anomaly in pure zinc.

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* The 810th report of the Research Institute for Iron, Steel and Other Metals.

(1) M. H. Le Chatelier, Compt. Rend., **111** (1890), 454.
(2) C. Benedicks, Metallurgie, **7** (1910), 531.
(3) M. Werner, Z. anorg. allg. Chem., **83** (1913), 275.
(4) C. Benedicks and R. Arpi, Z. anorg. allg. Chem., **88** (1914), 239.
(5) L. Holborn, Ann. Phys., **59** (1919), 145.
(6) Kathleen E. Bingham, J. Inst. Metals, **24** (1920), 333.
(7) W. B. Pietenpol and H. A. Milley, Phys. Rev., **34** (1929), 1588.
(8) G. Grube and A. Burkhardt, Z. Metallk., **21** (1929), 231.

Schulze[9], who previousely believed the existence of the transformations in zinc[10], reexamined the phenomenon with a spectroscopically pure zinc (99.993 per cent) and two impure ones, and found that the latter showed a few breakings but the former none.

The experimental investigations on the transformation of zinc had been made chiefly by measuring electric resistance, though other various properties were also utilized. Some of them were affirmative for its existence, while others negative. Later, X-ray method[11], which is capable of direct observation of the crystallographic change in metals, was applied to this problem during 1925~1934, and most results tended to the negative.

When the metallurgical investigation on zinc was in such a state as above, one of the present writers[12] began the study on the electron theory of metals, first with zinc. The main course was as follows:

The four nondiagram lines, $L\alpha'$, α'', β' and β'' of zinc measured by A. Karlson[13] were considered to be due to the transitions shown in Table 1. Here, E_1, E_2, E_3, and E_4, are the energy levels associated with the valence electron; the suffixes

Table 1. X-ray lines of zinc considered to be associated with valence electrons.

X-ray line	λ (Å)	ν/R^*	Transition
$L\alpha'$	12.190	74.755	L_{111}-E_2
$L\alpha''$	12.148	75.014	L_{111}-E_4
$L\beta'$	11.936	76.346	L_{11} -E_1
$L\beta''$	11.880	76.706	L_{11} -E_3

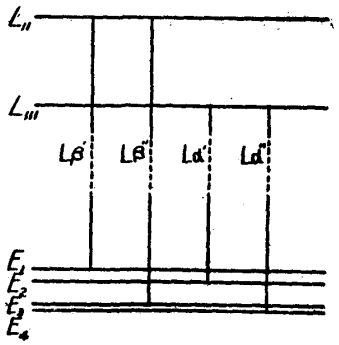

Fig. 1. Diagram illustrating the X-ray levels associating with valence electrons in zinc.

refer to the order of the energy as illustrated in Fig. 1. These transitions were suitably combined with the transitions[14], Kα_1, K-L_{111}; λ, 1432.174x, ν/R, 636.285 and Kα_2, K-L_{11}; λ, 1436.032x, ν/R 634.574, and the values K-E_1, K-E_2, K-E_3 and K-E_4 were obtained as shown in Table 2; in the similar way, K-$M_{IV,V}$ and K-M_V were obtained as shown together in Table 2. Further, from the above results, $M_{IV,V}$-E_3, E_1-E_3, M_V-E_4, E_1-E_4, E_2-E_3 and E_2-E_4 were computed and they were compared with photoelectric phenomena, obtaining the satisfactory agreements as

(9) A. Schulze, Z. Metallk., **22** (1930), 194.
(10) A. Schulze, Z. Metallk., **16** (1924), 48.
(11) W. H. Peierce, E. A. Anderson and P. van Dyck, J. Franklin Inst., **200** (1925), 349; J. R. Freeman, F. Sillers and P. F. Brandt, Scient. Papers Bur. Standards, **522** (1926), 661; F. Simon and E. Vohsen, Z. phys. Chem., **133** (1928), 165; E. A. Owen and J. Iball, Phil. Mag., **16** (1933), 479; E.A. Owen and E. L. Yates, Phil. Mag., **17** (1934), 113.
(12) M. Satô, Sci. Rep. Honda Anniv. vol. (1936), 136.
(13) A. Karlson, Ark. Mat. Astr. o. Fysik (A), **22** (1930), No. 9.
(14) Edlin, Zeits. Phys., **52** (1928), 364.
* The value R=109737.11 was used.

Table 2. Energy distance of $E_1 \sim E_4$, $M_{IV,V}$ and M_V from K.

$K-E_1$	$K-E_2$	$K-E_3$	$K-E_4$	$K-M_{IV,V}$	$K-M_V$
710.920	711.040	711.280	711.299	710.802	710.87

Table 3. Relations between the levels, $E_1 \sim E_4$ and photoelectric effect.

X-ray		Photoelectric		
$M_{IV,V}-E_3$	0.462	0.463	$\perp$ component	Selective maximum by polarized light[16].
E_1-E_3	0.360	0.338	$\perp$ component	
M_V-E_4	0.43	0.46	$\parallel$ component	
E_1-E_4	0.379	0.37	$\parallel$ component	
E_2-E_3	0.240	0.244	$\{10\bar{1}0\}$	Threshold for crystal surface[17].
E_2-E_4	0.259	0.263	{0001}	

shown in Table 3[15].

Thus, it was confirmed the energy levels E_1, E_2, E_3 and E_4 were of real existence. Further, it was inferred that the valence electrons in zinc would be in the energy states E_1, E_2, E_3 and E_4 (in Roman type) corresponding to the X-ray energy levels E_1, E_2, E_3 aud E_4 (in Italic type).

T. Fukuroi[18] studied the thresholds of the inner photoelectric effect of mercury, cadmium and zinc and confirmed that they were equal respectively to those of outer photoelectric effect. From this fact, it was inferred that[19] the electron in E_3 or E_4 is the "conduction electron" and that in E_1 or E_2, the "structure electron".

Next, the anomalous temperatures were considered[20]. Many workers, as briefly stated above, have observed anomalous changes at 170 and 320°C, the melting point 419°C being of course an anomaly. T. Fukuroi[21] found an anomaly at −26°C in the electric resistance of a thin film of zinc. These temperatures might be considered to form such a system that the adjacent intervals between them expressed in the absolute scale were in the ratio of 5 : 4 : 3 : 2. For molten zinc, experimental data on density, electric resistance, magnetic susceptibility, viscosity and vapour pressure were availed and it was found that 550, 796 and 905°C would be anomalous temperatures. Further, 200°C was assumed to be an anomalous temperature, forming a system together with the above three and the absolute zero. Then, the interval ratio of the above system became 4 : 3 : 2 : 1. Some workers have measured electric resistance, thermal expansion and shearing work of this metal in low temperature range. From these data, it was found that 36 and 90°K were anomalous tempatures, the interval ratio considered above being 2 : 3.

(15) M. Satô, Sci. Rep., **25** (1936), 771.
(16) F. Hlucka, Zeits. Phys., **92** (1934), 359.
(17) J.H. Dillon, Phys. Rev., **38** (1931), 408.
(18) T. Fukuroi, Sci. Pap. Inst. Phys. Chem. Resear., **32** (1937), 172.
(19) M. Satô, Sci. Rep. RITU, **2** (1950), 725.
(20) M. Satô, Sci. Rep., **27** (1939), 278; **28** (1939), 143.
(21) T. Fukuroi, Sci. Pap. Inst. Phys. Chem. Resear, **32** (1937), 196.

Zinc becomes a supra-conductor below 0.79°K. As the interval 0~0.79°K is very narrow, the existence of any anomaly within this range has not yet been reported. In the case of lead, however, it was found[22] that the thermal resistance in the supra-conducting range, 0~7.2°K, had a minimum at about 3°K, the interval ratio being 4 : 3. From this fact, it was assumed that 0.79°K was the highest anomaly of the lowest system of anomalous temperatures of zinc. The anomalous temperatures of zinc and the interval ratio are summarized in Table 4.

Table 4. Anomalous temperatures in zinc. The number in parenthesis is interval ratio.

Group	Anomalous temperatures in °K								
1	0	(4)	473	(3)	823	(2)	1069	(1)	1178
2	0	(5)	247	(4)	443	(3)	593	(2)	692 (m. p.)
3	0	(2)	36	(3)	90				
4	0		?		0.79	(t. p. of spra-cond.)			

From the facts that (1) the number of anomalous temperatures in each group, including 0°K, was odd; (2) the interval ratio was a sequence of simple natural numbers; (3) the temperature in the present case might be considered to be a measure of the energy of thermal vibration of zinc atom, it was concluded that the above regularity was, not only in formal but also in nature, identical with Landé's interval rule in the case of odd multiplicity in atomic spectra. Accordingly, it was inferred that the regularities in the groups 1, 2, 3 and 4, in Table 4, resulted respectively from L–S couplings of the valence electrons in E_1, E_2, E_3 and E_4. Further, from the interval ratio the total quantum number J was computed as shown in Table 5. From the relation, $L + S \geqq J \geqq |L - S|$, the values of L and S were obtained as shown in Table 6. Here, the relations, $L > S$ in E_2 and $L < S$ in E_3, were assumed. Thus, it was concluded that the energy states of the valence electrons in zinc in condenced states could be denoted by the spectroscopic notations as follows:

Table 5. Total quantum numbers of valence electron in zinc.

	Values of J				
E_1	4	3	2	1	0
E_2	5	4	3	2	1
E_3	1	2	3		
E_4		?			

Table 6. Values of L and S.

	L	S
E_1	2	2
E_2	3	2
E_3	1	2

E_1 : $^5D_{4,3,2,1,0}$ E_2 : $^5F_{5,4,3,2,1}$ E_3 : $^5P_{1,2,3}$

Here, the suffixes, the values of J, are written in the order of energy, that is, the former two are inverted and the latter is regular multiplet. As $S = 2$ in the above terms, the number of electrons associating with each of them must at least be 4.

(22) W. J. de Haas and A. Randemakers, Physica, 7 (1940), 992.

Accordingly, it was assumed that in this case 4 was real. Further, it was highly probable that the most outer electrons of zinc atoms in condenced states behave themselves as the valence electrons. Hence, it was inferred that each of the above terms, including that for E_4, was formed by two atoms. Thus, it appeared as if zinc atoms in condenced state form four kinds of diatomic molecules, but this was not in harmony with the experimental evidences, such as the activation energy in self-diffusion[23] and the sublimation energy[24]. Hence, it was inferred that the electrons in E_1 and E_4 belong to the same molecule (A_1, B_1) whereas those in E_2 and E_3 to another kind of molecule (A_2, B_2). Namely, the electrons in (A_1, B_1) and in (A_2, B_2) are respectively in oscillations which were denoted by $E_1 \rightleftarrows E_4$ and $E_2 \rightleftarrows E_3$, respectively.

To be kept from damping, these oscillations were, further, assumed to be in resonances with the neighbours in the group of the same kind of the molecules. Accordingly, the molecules in the group must be bound by the exchange energy of the resonating oscillations. Thus, the origin of the main part of the cohesive force in zinc crystal was explained to be the energies of the L–S coupling and of the resonating oscillations.

The above method of investigation was further applied to copper[25] and iron[26] and satisfactory results were obtained. For example, the ultimate origins of the transformations in iron, including the melting, and the other analogous phenomena were explained to be the transitions between the adjacent components of the multiplets which are similar to those of zinc.

From the above results, it may be concluded that all metals, probably without exception, have anomalous temperatures besides melting point, and these anomalies are ultimately caused by electron transitions. In the special case in which the transition affects the binding force between atoms so strongly that the crystallographic structure is changed, the anomaly is the so-called transformation. From this view-point, no basic difference exists between the so-called transformation and the anomaly allied to the former. Hence, from the electronic point of view, anomaly as stated above may appropriately be called the "transformation".

From the result of the above considerations, the previous investigations mentioned in the initial part of this chapter reviewed, and it was concluded that though the experimental confirmation is not yet satisfactory, the anomaly really exists in zinc. If a suitable method is adopted, the confirmation will be certain in success. So, it was decided to ascertain it by the precise measurement of the temperature dependence of the electric resistance of zinc.

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(23) M. Satô, Sci. Rep., **31** (1942), 38.
(24) M. Satô, Sci. Rep., **31** (1943), 153.
(25) M. Satô, Sci. Rep. RITU, **2** (1950), 424, 726 ; **3** (1951), 661 ; **5** (1953), 533 ; **6** (1954), 458 ; **7** (1955), 56.
(26) M. Satô, Sci. Rep. RITU, **4** (1952), 597.

II. First experiment

1. Specimen

The specimens were made of the zinc obtained from Tadanac Co., Canada, and were of wire form, 1 mm in diameter. The impurities were copper, iron and lead, being respectively, 0.0014, 0.0026 and 0.0039 per cent, with a trace of cadmium.

2. Apparatus

The resistance measurements were made by a standard potentiometric method using a low voltage potentiometer and a galvanometer of the sensitivity of 0.44 μV. The temperature was measured with this potentiometer, using a Pt-PtRh thermocouple calibrated within ± 0.05°C. A resistance furnace, 4 cm in inner diameter and 70 cm in length was used; a metal tube was inserted into the furnace to unify the temperature distribution. The distribution was uniform within ± 0.4°C at 200°C, or within ± 1°C at 500°C, throughout the central range of 40 cm.

The specimen, 80 cm in length, was connected with the current and potential leads as shown in Fig. 2. In this figure, A_1 and A_2 are copper long cylinder with the section of a sector, a little larger than the quadrant; the length of each cylinder was 44 cm and the radius of the sector, 0.5 cm. Four pieces of copper wire (c_1, p_1) and (c_2, p_2) were tightly soldered respectively to A_1 and A_2 as illustrated in the figure. The specimen s was bent smoothly in the middle portion and each branch was inserted into a quartz tube, about 38 cm in length. The ends of the specimen pushed out of the quartz tube were respectively soldered to p_1 and p_2 as shown in the figure. Accordingly, c_1 and c_2 were the current leads and p_1 and p_2 the potential leads. The solder was prepared by adding zinc to a commercial solder of Pb-Sn system; the temperature of beginning of solidification was about 380°C. The system shown in Fig. 2 was bundled together with another thin quartz tube in the way as the sectional view is shown in Fig. 3; thermojunction j was inserted into the quartz tube. The above bundle was rolled round by a ribbon of thin mica, tied up by thin copper wire passing on the mica and inserted into a quartz tube, 1.3 cm in inner diameter and 100 cm in length; the quartz tube was inserted into the furnace. To keep the specimen and the lead wire system from further oxidation as well as sublimation, hydrogen gas, 99.5 per cent in purity, was further purified and streamed through the quartz tube in atomospheric pressure.

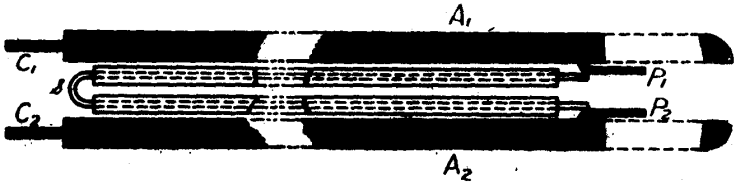

Fig. 2. Schematic illustration showing the connection of specimen with lead wires.

Fig. 3. Sectional view of the bundle binding the specimen, thermojunction and their holders.

Special precautions were paid to minimize the thermoelectric disturbance.

Whole apparatus was set in a dark compartment of suitable size. In order to avoid thermal convection, the space in the compartment was suitably divided into several sections by black curtains. Two small heaters, miniature lamps, were respectively set near the potentiometer terminals in the galvanometer circuit, and by adjusting the heating currents, the thermoelectric disturbance in the circuit was almost eliminated. By the above devices the thermoelectromotive force in the whole circuit could be diminished to 2~3 μV, and it was kept almost constant during a run of the measurement, the duration being 7~8 hours.

3. Procedure

The current in the specimen was generally about 60 mA. As the current varied from moment to moment, its momentary value was presicely measured by the usual method, at about every five minutes; the accuracy was 1 μA. Accordingly, the accurate value of the current at any time in the measurement was obtainable by interpolation.

The temperature was raised or lowered in the rate of about 2°C per minute. The temperature and the potential difference between the terminals of the specimen were measured alternately by the same potentiometer, the interval being about 20~30 seconds; the potentials ranging in 3~10 mV were read down to 10^{-4} mV. In the temperature range within which no anomaly was expected to exist, the electromotive force corresponding to every measured temperature was computed by interpolation from the two adjacent values. The current at the moment when the temperature was observed was obtained as mentioned above. Thus, corresponding to the temperature the resistance was obtained, the temperature interval between two adjacent measured points being generally about 2°C. In the temperature range within which the anomaly was expected to exist, the temperature corresponding to the measured value of the electromotive force was also computed by the method similar to that described above. Accordingly, in this case the temperature interval between adjacent measured points was about 1°C. The experimental error of the resistance thus computed was estimated to be within 0.03 per cent.

4. Results

In order to see the resistance change during the measurements in heating and cooling, the ratio,

$$\sigma = r/r_0$$

was always considered, where r and r_0 are the resistances in the heating at t° and 20°C respectively. Further, to visuarize the anomalous change of σ, the experimental result was illustrated as follows: The equation of the straight line passing through two points (20°, 1) and (300°, σ_1) in the (t, σ) diagram is

$$\frac{\sigma' - 1}{t - 20} = \frac{\sigma_1 - 1}{300 - 20} \quad \text{or} \quad \sigma' = \frac{(\sigma_1 - 1)(t - 20)}{280} + 1$$

Here, (t, σ') are the coordinates of a current point on the straight line. From the above equation, the value of σ' corresponding to each value of σ was computed,

$$\Delta\sigma = \sigma - \sigma'$$

was plotted as the function of t; this shows the deviation of σ (t) curve from linearity. The typical curves are shown in Fig. 4.

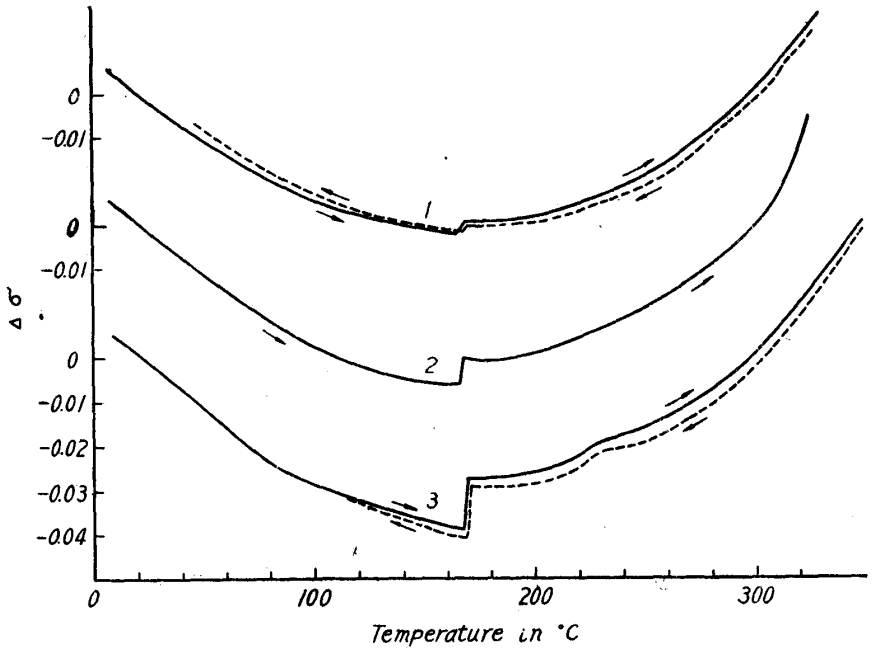

Fig. 4. $\Delta\sigma$-t curves showing discontinuous change of resistance at 170°; 1, slowly cooled from 320°C in the furnace; 2, annealed at 330°C for 24 hours; 3, annealed at 330°C for 48hours.

In these curves, the anomaly at 170°C obviousely appears; the value of σ changes discontinuously and reversely; the changes of the resistance in the curves 1, 2 and 3 amount respectively to 0.3, 0.5 and 1.2 per cent of the value at room temperature. Hence, it may be inferred that the anomaly is a transformation, even in the classical sense.

But, the anomaly at 320°C does not evidently appear in the figure. So, the straight line passing through two measured points (250°, σ_1) and (350°, σ_2) was selected as the standard line and obtained the results as shown in Fig. 5. In this figure, the latter anomaly appears though very faintly.

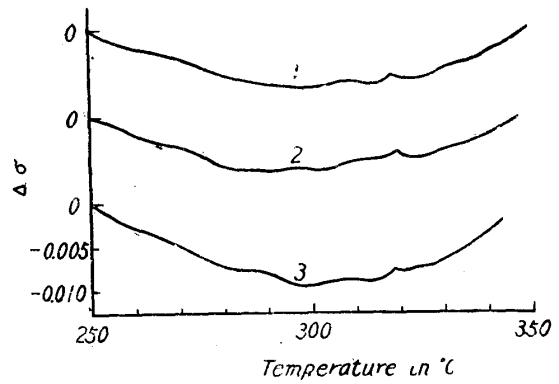

Fig. 5. $\Delta\sigma$-t curves showing anomalous change of resistance at 320°C; 1, slowly cooled from 350°C; 2, annealed at 330°C for 24 hours; 3, annealed at 330°C for 48 hours.

Besides above two anomalies, it is seen at 230°C in 3 of Fig. 4. In the present experiment, the heating and cooling were repeated nine times with the same specimen; before and after the fifth run, the specimen was annealed at 330°C for 24 hours. Until the fifth run, the above anomaly did not appear, but from the sixth it appeared as shown in Fig. 6. From these facts, it was seen that long annealing was

necessary for the appearance of this anomly.

Now, during the course of the first experiment, it became questionable that the solder might affect the appearance of the anomaly. So, the second experiment was carried out.

III. Second experiment

In this case, another solder of Zn-Sn system was used; its beginning point of solidification was about 380°C. The specimen, apparatus etc. were all the same as in the first experiment. The result is shown in Fig. 7. In this figure, the anomaly evidently appears at 200°C, but not at 170°C.

From the above results, it was evidently seen that the appearance of the anomaly was affected by the solder.

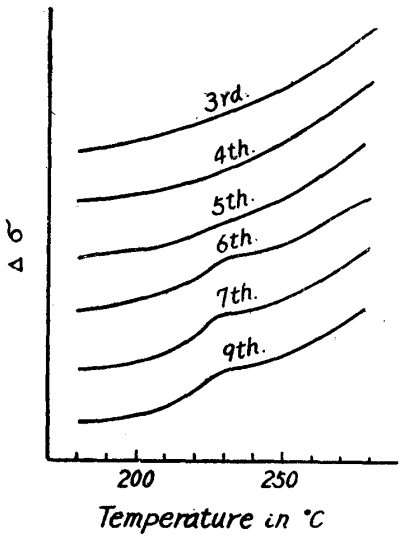

Fig. 6. $\Delta\sigma$-t curves showing the condition for the appearance of the anomaly at 230°C.

IV. Explanation

In order to clarify the above effect, the thermal analysis of the solder of Pb-Sn-Zn system was made and the cooling curve was obtained as shown in Fig. 8. In this curve, a stationary point at 170°C and a bend at 228°C are seen. These points may be considered to correspond respectively to the anomalies at 170°C (Fig. 4) and 230°C (Figs. 4, 6). Further, referring to the equilibrium diagram of Pb-Sn-Zn system[27], in which the eutectic point is 177°C, it may be inferred that the former point was eutectic temperature of the solder. From the condition of appearance of the latter anomaly, the running feature of the curve in Fig. 8 at 228°C and the above equilibrium diagram, this anomaly seems to correspond to the temperature of second separation in the solder.

Next, from the equilibrium diagram of Sn-Zn system[28], in which the

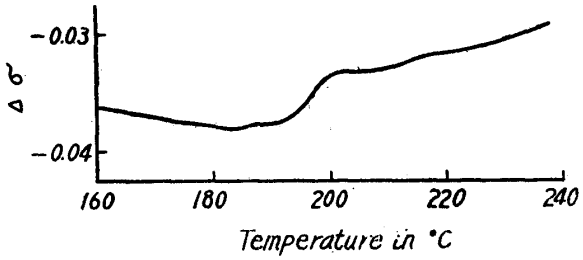

Fig. 7. $\Delta\sigma$-t curve, when the solder of Sn-Zn system was used.

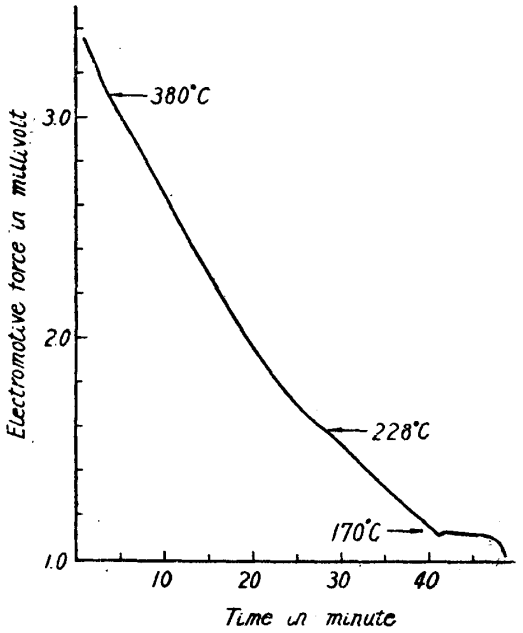

Fig. 8. Cooling curve of the solder of Pb-Sn-Zn system.

(27) Metals Handbook (1948), 1268.

(28) M. Hansen, *Der Aufbau d. Zweistofflegierungen* (1936), 1081.

eutectic point is 199°C, the anomaly at 200°C in Fig. 7 may be explained as to be due to the eutectic phenomenon in the solder. Finally, from the equilibrium diagram of Zn-Pb system[29], in which the temperature of the eutectic point in lead rich side is 318°C, the anomaly at 320°C in Fig. 5 may be explained as to be due to the eutectic phenomenon taking place in the specimen, because the specimen contains 0.0039 per cent of lead as stated in II, A. Thus, all anomalies observed in the present experiments were satisfactorily explained as to be due to the effects of the solders and the impurity contained in the specimen.

Of these temperatures, however, 170, 318 and 199°C are respectively in agreement with 443, 593 and 473°K in Table 4; the former two and the latter, belonging respectively to the groups 2 and 1, satisfy Landé's interval rule; but no temperature in this table corresponds to 230°C. That is, the former three can theoretically be considered as characteristic to zinc, but the latter cannot. These facts may be explained as follows:

Take an alloy at a point under the eutectic line in the Sn-Zn system, and suppose that the temperature was raised and reached the eutectic temperature 199°C, then either or both of metals must begin to melt from the contact surface. This melting, however, must caused by the electron similar to the case of melting of an isolated pure metal. If this is the case, the transition E_1: $^5D_4 \rightarrow {}^5D_3$, which was expected to occur in zinc at 200°C in heating, may be the one considered above. Thus, the eutectic temperature 199°C must be an anomalous temperature of pure zinc. In the same way, the eutectic temperatures, 170° and 318°C, may be considered to be anomalies of pure zinc corresponding to the terms, E_2: $^5F_3$ and $^5F_2$, respectively. Here must be added a remark. The theoretical value of the former anomaly, that is, the point dividing the interval, 0°K~419.4°C, m.p., in the ratio(5 + 4) : (3+2) is 172.3°C. The difference between this and 177°C, the eutectic temperature of Pb-Sn-Zn system, cannot be considered to be within experimental error. This fact will be explained in the same way when the equilibrium diagram will be clarified in more detail. Finally, 230°C will be considered. If the above explanation for this temperature is correct, its value must depend on the composition of the alloy. Accordingly, it cannot be characteristic of zinc, that is, this is not the anomaly of zinc.

Summary

(1) Precise measurements of the electric resistance of pure zinc were made at high temperatures and anomalous changes were observed at 170, 200, 230 and 320°C.

(2) The anomalous temperatures 180°, 200° and 320°C were respectively the eutectic temperatures of the solders of Pb-Sn-Zn and Sn-Zn systems, and of the alloy of Pb-Zn system, formed in the specimen.

(3) From a conception of the eutectic phenomena, these temperatures were explained to be the anomalous temperatures of zinc itself.

(29) Ditto, 1008.