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**DEPARTMENT OF COMMERCE**  
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George K. Burgess, Director

**PURE ZINC AT NORMAL AND  
ELEVATED TEMPERATURES**

By John R. Freeman, jr., Frederick Sillers, jr.,  
and Paul F. Brandt

SCIENTIFIC PAPERS OF THE BUREAU OF STANDARDS, No. 522



DEPARTMENT OF COMMERCE  
BUREAU OF STANDARDS  
George K. Burgess, Director

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SCIENTIFIC PAPERS OF THE BUREAU OF STANDARDS, No. 522  
[Part of Vol. 20]

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# PURE ZINC AT NORMAL AND ELEVATED TEMPERATURES

## Part I. SOME PHYSICAL PROPERTIES

BY

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## Part II. CRYSTAL STRUCTURE

BY

FREDERICK SILLERS, Jr., Scientific Aid  
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April 3, 1926



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# PURE ZINC AT NORMAL AND ELEVATED TEMPERATURES

By John R. Freeman, jr., Frederick Sillers, jr., and Paul F. Brandt

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## ABSTRACT

A study has been made of the physical properties and crystal structure of pure zinc. Data are given on the following properties: Coefficient of expansion, density, scleroscope and Brinell hardness, and tensile properties and crystal structure at normal and elevated temperatures. Proof is given that zinc has but one allotropic form between normal temperatures and the melting point.

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## PART I

### I. INTRODUCTION

The Bureau of Standards was requested by the New Jersey Zinc Co. to determine the physical constants of chemically pure zinc which they had succeeded in producing in relatively large quantities. This proposed work was in accordance with an established policy of

the bureau to study the properties of pure metals when available, and was therefore undertaken on recommendation of the Nonferrous Metals Advisory Committee to the Bureau of Standards. Further, in view of the exceptional purity of the zinc, the bureau considered it desirable to investigate at the same time the alleged allotropy which had been reported by several investigators. In a paper on this subject presented in 1920 by Miss K. E. Bingham,<sup>1</sup> a very complete review and critical discussion is given of the work of previous investigators. It is therefore considered unnecessary to give a further discussion and review of this earlier work but to confine the discussion here to a brief review of the more recent work<sup>2</sup> and to point out the reasons for the very marked difference in the conclusions drawn from the work reported here and that of the previous investigators. In general, the latter concluded that zinc occurred in three allotropic forms.

All previous work had been carried out on worked material. It was therefore thought desirable at this time to work insofar as possible with cast material only.

## II. PURITY OF ZINC USED

A spectroscopic examination<sup>3</sup> was made and the arc spectra showed the sample to contain no magnesium, antimony, tin, silicon, calcium, or mercury. Lead, iron, and cadmium were detected in very minute quantities. There was a trace of copper, but certainly less than 1 part in 1,000,000.

Chemical analysis<sup>4</sup> showed the impurities to be as given in Table 1.

TABLE 1.—*Composition of zinc*

Element	Per cent
Lead.....	0.001
Cadmium.....	.003
Iron.....	.003
Arsenic.....	Less than 0.00001.
Copper.....	} Not detected.
Tin.....	
Antimony.....	

## III. PHYSICAL PROPERTIES

The following properties were determined: Thermal expansion, density, hardness, tensile properties, and microstructure.

<sup>1</sup> K. E. Bingham, The allotropy of zinc, *Jour. Inst. Metals*, 2, p. 333; 1920.

<sup>2</sup> L. Losana, Sull' allotropia dello zinco. *Gazetta Chimica Italiana*, 53, No. 8, p. 539, 1923. Eastman, Williams, and Young, The specific heats of Mg, Ca, Zn, Al, and Ag at high temperatures. *Jour. Am. Chem. Soc.*, p. 1178; May, 1924.

<sup>3</sup> By W. F. Meggers, Bureau of Standards.

<sup>4</sup> By J. A. Scherrer, Bureau of Standards.



1. THERMAL EXPANSION <sup>5</sup>

A specimen 30 cm long and 0.714 cm (9/32 inch) diameter was cast by drawing the molten metal up into a glass tube. The linear expansion was then determined according to standard practice <sup>6</sup> at the Bureau of Standards.

Particular attention was paid to determining any marked change in rate of expansion in the region of 170° C., the temperature of the supposed lower allotropic transformation as reported by Bingham

On neither of two heating cycles to 250 and 300° C., respectively, was there any evidence of a transformation point as determined by plotting the data for these two heating cycles, which are given in detail in Table 2, as it is impractical to plot to the desired scale in publication. The average coefficients of expansion are given in Table 3.

TABLE 2.—Expansion observations on sample

First test		Second test	
Tem- pera- ture	$\Delta l$ <sup>1</sup>	Tem- pera- ture	$\Delta l$ <sup>1</sup>
° C.	$\times 10^{-6}$	° C.	$\times 10^{-6}$
20.2	0	20.1	0
100.3	3, 159	102.3	3, 188
151.1	5, 191	150.0	5, 092
162.1	5, 627	177.5	6, 170
166.8	5, 827	201.3	7, 133
170.0	5, 951	251.7	9, 132
175.1	6, 155	297.7	10, 917
179.9	6, 341	310.4	11, 467
190.6	6, 762	143.6	4, 766
203.1	7, 259	27.5	128
252.8	9, 232		
143.0	4, 781		
26.2	190		

<sup>1</sup> Represents the change per unit length from the length at the initial temperature.

After the first test the specimen was 0.004 per cent shorter than its original length at 20.2° C. and after the second test it was 0.014 per cent shorter than its length at the start of the second test at 20.1° C. That is, on two successive heatings to approximately 250 and 310° C., respectively, the cast bar had decreased in length a total of approximately 0.018 per cent. It is suggested that this shortening may be due to the fact that the structure of the expansion test bar changed, as described below, from a polycrystalline structure, typical of cast material, to one of a few very large crystals.

<sup>5</sup> By W. Souder and P. Hidnert, Bureau of Standards.

<sup>6</sup> A brief description of the apparatus is given in B. S. Sci. Paper No. 497, Thermal Expansion of Aluminum and Various Important Alloys, P. Hidnert.

TABLE 3.—Average coefficient of expansion of pure zinc

Temperature range (°C.)	Average coefficient of expansion per degree centigrade $\times 10^6$	
	First heating	Second heating
20 to 100.....	39.5	38.7
20 to 150.....	39.6	39.2
20 to 200.....	39.7	39.3
20 to 250.....	39.7	39.4
20 to 300.....		39.3

On a third heating to 350° C. in an attempt to locate the alleged transformation at 330 to 340° C., the sample bent and after cooling to room temperature it was found to fracture under its own weight when held in a horizontal position. The fracture was always very smooth and had a mirrorlike surface suggestive of the fracture of single crystal wire described by Mark.<sup>7</sup> Photographs of a fractured end of the sample from which the specimen was taken and of the specimen after the change occurred are shown in Figure 1 (*a*) and (*c*), respectively. The latter is quite similar to photographs of fractures shown in the article referred to in footnote 7. The angle of the fracture in this specimen was always either at 45° or at 90° to the axis. The short sections shown in Figure 1 (*c*) were readily obtained by prying them off with the point of a knife. This change in structure shown in Figure 1 (*b*) and (*d*) is probably the result of the annealing consequent to the thermal expansion test, following casting strains or slight strain from straightening put in the zinc during preparation of the specimen for test.

These expansion-test results are quite at variance with the dilatation experiments reported by Losana,<sup>8</sup> who found marked changes at 174 and 315° C., the lower point apparently confirming the results of Bingham's<sup>9</sup> density determinations on specimens quenched from elevated temperatures.

The zinc used by Losana was of the following composition: Tin, 0.023 per cent; lead, 0.029 per cent; iron, 0.043 per cent; cadmium and copper, traces; zinc, 99.87 per cent. The zinc-tin eutectic, containing approximately 16 atomic per cent of zinc<sup>10</sup> melts at 197° C. The lead-tin eutectic<sup>10</sup> melts at 180° C. In view of these facts and the presence in the zinc of a small amount of iron, it is suggested that the transformations observed by Losana may have been due to the impurities.

<sup>7</sup> Mark, Polanyi, and Schmid, Vorgänge bei der Dehnung von Zink-Kristallen, Zeit. für Physik, **12**, p. 58; 1922.

<sup>8</sup> See footnote 2, p. 662.

<sup>9</sup> See footnote 1, p. 662.

<sup>10</sup> Desch, C. H. Metallography. 3d ed.; p. 403.

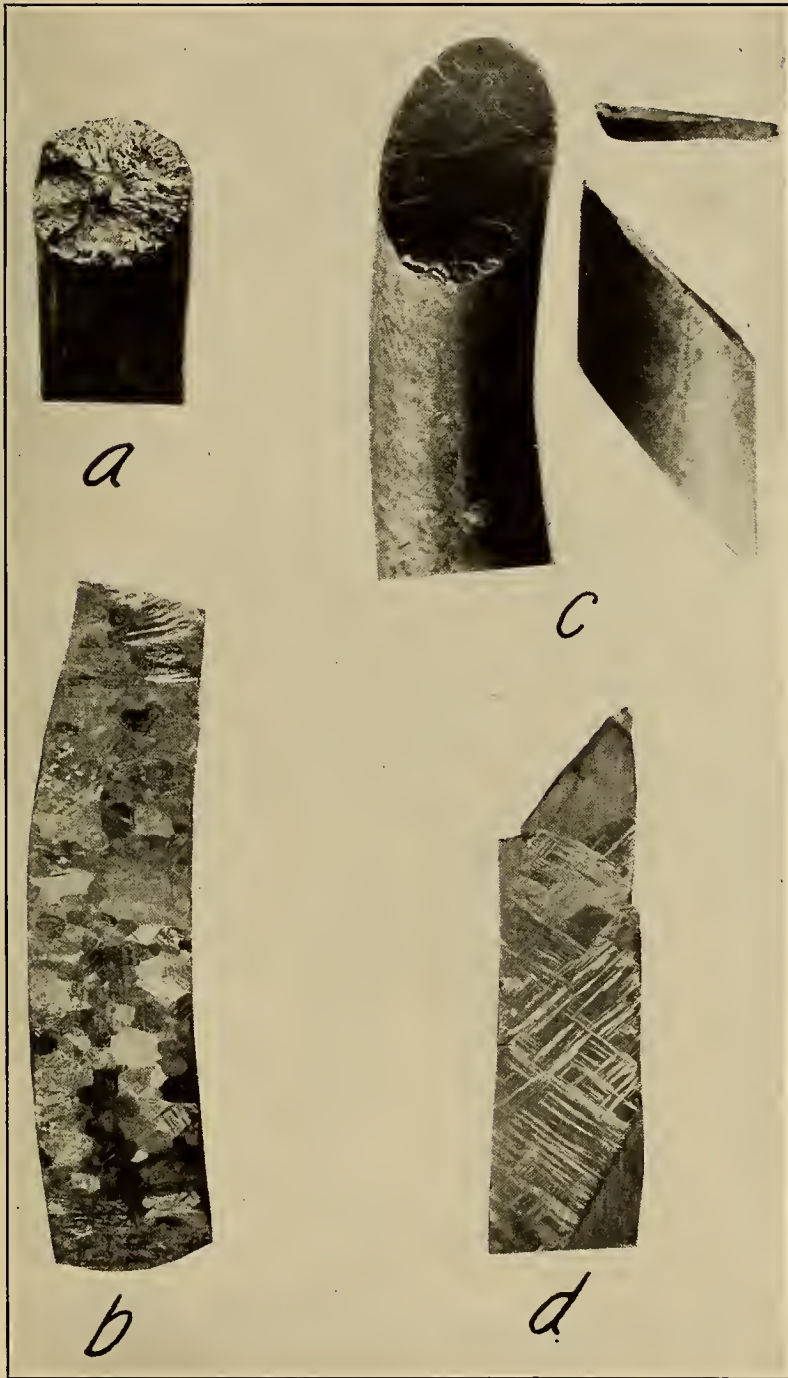


FIG. 1.—Fracture and macrostructure of thermal expansion specimens before and after test

- a. Fractured end of thermal expansion specimen before test.
  - b. Polished and etched section of a specimen with a fracture similar to a.
  - c. Fractured portions of the specimen shown in a after test.
  - d. Polished and etched section of specimen showing fracture similar to c.
- Etching reagent: 5 per cent alcoholic hydrochloric acid.  $\times 2\frac{1}{2}$ .

## 2. DENSITY

The specimens used for the determination of the density under different conditions of heat treatment were obtained by casting a tensile test bar as described under mechanical tests. The reduced section was then cut into small disks about one-fourth inch thick. Strains incident to the machining operations were removed by heating the specimens in an oil bath for one hour at 150° C. and letting them cool in the bath to room temperature. The individual specimens were then heated to the desired temperature, held 15 minutes at temperature, and then quenched in water. The densities<sup>11</sup> of the several specimens were determined in the volumetric laboratory of the Bureau of Standards, their standard practice being used.

The results of these determinations, together with the quenching temperatures, are given in Table 4.

TABLE 4.—Density and hardness of pure zinc

Specimen number	Quenching temperature	Density at 25° C.	Scleroscope hardness	Rockwell hardness reading on C scale one-eighth inch ball, 60 kg, one minute
	° C.	g/cm <sup>3</sup>		
20.....	20	7.130		97
4.....	61	7.132	8.8	107
5.....	94	7.131	9.4	
23.....	120	7.134		
6.....	142	7.125	9.2	
24.....	145	7.130		
7.....	154	7.132	8.2	110
8.....	158	7.133	7.6	
9.....	163	7.132	8.6	
15.....	171	7.130	7.8	
13.....	180	7.129	9.0	102
14.....	190	7.130	9.0	
11.....	212	7.129	9.4	
10.....	237	7.130	9.6	
12.....	267	7.133	8.8	107
16.....	285	7.130	9.2	
17.....	289	7.131	8.8	
18.....	302	7.131	8.0	
19.....	342	7.131	9.2	116
28.....	( <sup>1</sup> )	7.132		106

<sup>1</sup> Cooled in crucible.

It is evident from the data that there is no change in the density due to quenching at increasingly higher temperatures. The value 7.125 for the specimen (No. 6) quenched from 142° C. is a little lower than the others, but in view of the very consistent agreement in all other cases it is probable that there was a very minute blowhole in

<sup>11</sup> By E. L. Peffer and E. E. Hill. The apparatus used is described in Bulletin of the Bureau of Standards 9. The Density of Ethyl Alcohol and Its Mixtures with Water. In this case the samples were immersed in a kerosene bath held at a constant temperature of 25° C.

this particular specimen. A duplicate test (No. 24) was made which proved the above assumption.

These results do not check the similar series of determinations reported by Bingham,<sup>12</sup> who found a sharp change in specific gravity at 170° C., while no such change was noted in the present experiments. Peirce,<sup>12</sup> in a discussion of Miss Bingham's paper, called attention to the marked deviation of the density values reported by Miss Bingham from results obtained by him in the laboratories of the New Jersey Zinc Co. It is of interest to note that the average density, 7.139 g/cm<sup>3</sup> obtained by averaging the data given in Table 1 of Miss Bingham's paper is in close agreement with the values 7.135 to 7.150 g/cm<sup>3</sup> obtained by Peirce. The average value of data given in Table 4 of this report is 7.131 g/cm<sup>3</sup>.

These small differences may be attributed to the fact that the determinations reported by Bingham and by Peirce were made on rolled zinc while the data reported here were obtained on cast zinc, or possibly to the difference in the temperature at which the tests were made, as neither Bingham nor Peirce state the temperature of test

### 3. HARDNESS TESTS

(a) **SCLEROSCOPE HARDNESS TESTS.**—Scleroscope hardness tests were made on the same specimens used for the density determinations. A Shore recording type of scleroscope was used. Five readings were taken on each specimen and the averages thus obtained are also given in Table 4. On individual specimens the hardness varied in several cases as much as 3 or 4 points and in no case was the variation less than 2 points. Inasmuch as the maximum variation between the average values for all specimens is only 2 points, the authors conclude that quenching at different temperatures has no effect on the scleroscope hardness of pure cast zinc.

Hardness tests were also made in a Rockwell machine using a one-eighth inch diameter ball and 60 kg load applied for one minute. The same specimens used for the scleroscope hardness and density determinations were used. The results obtained are also given in Table 4. Two readings were taken on each specimen and the average of these is the value given. These individual readings varied from 5 to 9 points. It is evident from the data that, within experimental error, there is no change in Rockwell hardness of pure cast zinc annealed and quenched from elevated temperatures.

Peirce pointed out that the scleroscope hardness of pure zinc varies considerably with the orientation of the grain. The authors believe that a similar effect, together with variation in grain size, explains the wide variation found in the Rockwell hardness values.

<sup>12</sup> See footnote 1, p. 662.

(b) **BRINELL HARDNESS TESTS.**—Brinell hardness tests were made at elevated temperatures on specimens of cast zinc. A standard alpha Brinell machine was used with a 10 mm ball and a 500 kg load applied for 30 seconds. The specimens were obtained by casting disks 2 inches in diameter and about one-half inch thick in a steel mold. All specimens were annealed at 150° C. before hardness tests were made.

The specimens were heated during test in an electrically heated oil bath in which the specimen was immersed throughout the period of test. They were brought up to the desired temperature and held at that temperature for 15 minutes before testing to insure uniformity of temperature throughout the specimen. Three impressions were made on each specimen at each temperature at equidistant points on a circle one-half the radial distance from the center to the edge of the disk. The average of these three independent determinations was taken as the Brinell hardness value. The results are given in Table 5.

TABLE 5.—*Brinell hardness of pure zinc at elevated temperatures*

Temperature of test	Brinell hardness —10 mm ball, 500 kg load applied 30 seconds
° C.	
20	31.0
110	19.0
120	18.5
130	16.3
140	15.5
150	13.0
160	12.5
170	10.5
180	9.0
190	7.5
200	6.5

In each case the edge of the impression was quite irregular, making it difficult to measure the diameter very exactly, and for temperatures above 200° C. the diameter of the impression approached the diameter of the ball due to the extreme softness of the metal at this relatively high temperature. It is unfortunate that satisfactory readings could not be obtained at a temperature somewhat higher than the temperature of the supposed lower allotropic change, but it is quite evident from the data that there was no marked change in hardness over the temperature range studied within the limits of error of the method of measurement.

#### 4. TENSILE PROPERTIES

(a) **TENSILE TESTS.**—Tensile tests were made on cast specimens at normal and elevated temperatures. The test specimens were made by pouring the molten zinc at a temperature of 430° C. into the steel

mold shown in Figure 2. This mold was previously dressed by wiping with oily waste, then making several castings of a zinc of somewhat lower grade than the pure zinc used in these experiments. After the temperature of the mold had been raised in this manner to a temperature sufficient to prevent cold shuts, the desired number of castings of the very pure zinc were poured. The castings were always removed from the mold while hot. Care was taken at all times to prevent contamination of the zinc. Standard 0.505-inch diameter tensile test bars with 2-inch gauge lengths and threaded ends were then machined from the castings. After machining and previous to testing all tensile bars were annealed to remove any casting strains that might be present by heating at 150° C. in an oil bath for one hour and then letting them cool to room temperatures in the bath. As discussed later in the paper, this treatment had a very important and unexpected influence on the tensile tests.

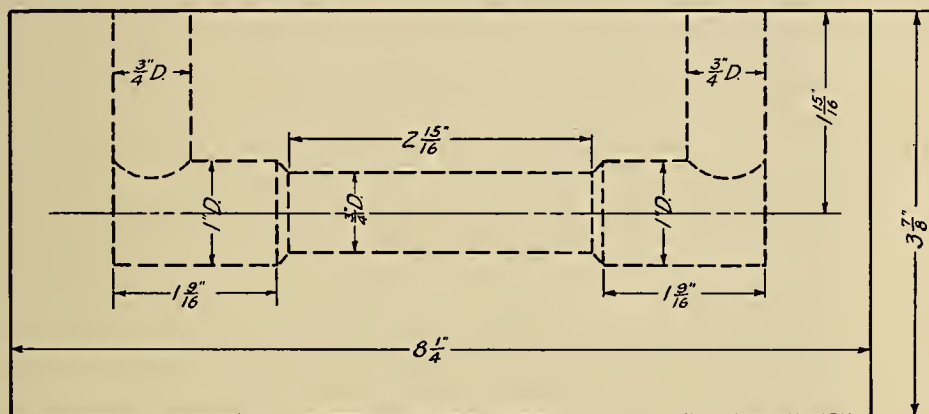


FIG. 2.—Mold for tensile test specimens

The tensile tests were all made in a standard Riehle 10,000-pound testing machine, the 1,000-pound total capacity range being used. The specimens were heated at the desired temperature during test in a specially constructed oil bath which was heated electrically and permitted very close temperature control. Uniformity of temperature throughout the bath was obtained by constant mechanical stirring of the oil. Measurement showed the maximum gradient in the bath to be less than 5° C. In most cases the specimen to be tested was heated up to temperature in the bath from room temperature. It was held in all tests at the desired temperature for from 10 to 15 minutes and the tensile test then made with the specimen immersed in the oil. The rate of loading was in every test 0.06 inch a minute and was maintained constant throughout the test until failure occurred.

The results of the tensile tests are given in Table 6. Two series of tests were made. Photographs of the first series of specimens after failure are shown in Figure 3 and the second series in Figure 4.

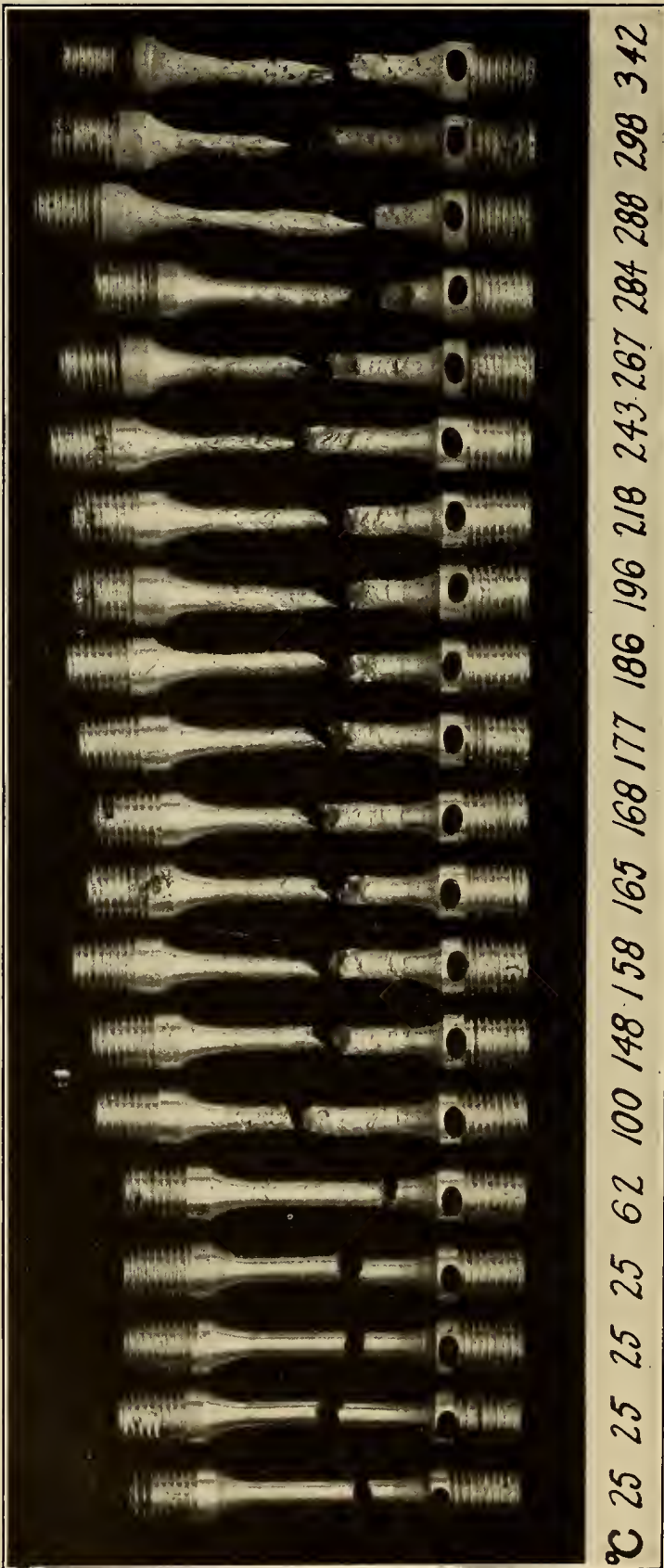


FIG. 3.—Tensile test specimens of pure zinc tested at elevated temperatures (first series)  $\times \frac{3}{8}$





FIG. 4.—Tensile test specimens of pure zinc tested at elevated temperatures (second series)  $\times 1\frac{1}{8}$

In these photographs one end of each bar has been turned at right angles to its mate in order to show better the characteristics of the fracture.

TABLE 6.—Results of tensile tests

Specimen No.	Tempera- ture of test	Ultimate strength	Elonga- tion in 2 inches	Type of fracture
	° C.	Lbs./in. <sup>2</sup>	Per cent	
1 <sup>1</sup> -----	25	2,890	-----	Brittle. <sup>2</sup>
2 <sup>1</sup> -----	25	4,170	-----	Do.
3-----	25	4,010	2.0	Do.
4-----	25	4,220	2.5	Do.
6-----	62	5,180	7.0	Do.
21-----	62	6,050	-----	Do.
32-----	95	3,700	-----	Do.
7-----	100	5,840	28.0	Oblique.
24-----	142	4,150	-----	Do.
8-----	148	4,180	25.0	Do.
23-----	154	4,340	-----	Do.
12-----	158	3,960	40.0	Do.
17-----	163	3,510	28.0	Do.
25-----	163	4,200	-----	Do.
15-----	168	3,590	26.0	Do.
27-----	170	3,650	-----	Do.
13-----	177	3,490	40.0	Do.
11-----	186	3,120	42.0	Do.
5-----	196	3,140	38.0	Do.
26-----	200	3,000	-----	Do.
16-----	218	2,390	45.0	Do.
9-----	243	1,880	70.0	Wedge.
28-----	250	1,800	-----	Do.
18-----	267	1,390	60.0	Do.
29-----	280	1,200	-----	Do.
22-----	284	1,200	81.0	Do.
10-----	288	946	34.0	Do.
19-----	298	896	60.0	Do.
30-----	300	950	-----	Do.
20-----	342	500	56.0	Do.
31-----	350	450	-----	Do.

<sup>1</sup> Not annealed at 150° C. before test.

<sup>2</sup> By "brittle fracture" is meant a fracture characteristic of a brittle cast structure.

(b) TYPES OF FRACTURE.—The photographs show the very marked changes in the appearance of the fractured specimens that were obtained with increasing temperature of test. At normal temperatures the fracture was characteristic of that of a brittle cast structure, and when viewed vertically the typical radial grains of a cylindrical casting were evident. At approximately 60° C. the material was still quite brittle, but there was a noticeable crinkling of the surface of the specimen along the entire gauge length. With increasing temperatures this crinkling increased and was accompanied by a very marked increase in elongation. The character of the fracture also changed. Its surface made an oblique angle with the axis of the specimen and had a "fish-scale" appearance. The reduction in section of the specimen was not symmetrical, but was principally along one diameter, as is evident in Figures 3 and 4. At temperatures approaching 240° C. another marked change in the character of the fracture became apparent, and at temperatures

above 240° C. it had changed completely from the single plane oblique to the major axis of the specimen to a pair of planes forming at the more elevated temperatures a very sharp symmetrical wedge. The reduction of section took place almost entirely along the diameter perpendicular to the edge of the wedge.

The elongation in this higher temperature range was markedly greater than that in the intermediate temperature range, which in turn was very much greater than that obtained at temperatures below approximately 100° C.

There appeared then to be three characteristic fractures typical of three temperature ranges which, for the conditions of test here reported, may be roughly placed as follows: 25 to 100° C., brittle fracture; 100 to 240° C., oblique fracture; 240° C. to melting point, wedge fracture. The line of demarcation, however, between the temperature ranges stated above is not sharp, the change from one type of fracture to the next being rather gradual.

(c) MICROSTRUCTURE.—In Figure 5 (a), (b), (c), (d) are shown polished and etched surfaces of specimens Nos. 20, 7, 12, and 19, which were used for the density and hardness determinations (Table 4). Care was taken in polishing and etching these specimens in order to make sure that the structures shown were characteristic and that the small grains apparent in the macrograph were not a surface effect. It is believed that the circular band of small grains visible in Figure 5 (a) is the result of recrystallization occurring on annealing the strained material, the strains having been set up during the machining of the bar. This is similar to the well-known germination which occurs in a mild steel on annealing.<sup>13</sup> The partial recrystallization which has taken place in the other specimens is probably due to similar causes. Undoubtedly shrinkage stresses are set up in the casting which are of sufficient magnitude to cause subsequent recrystallization, particularly at the higher annealing temperatures. It will be noted, however, that even in specimen 19 (fig. 5 (d)) evidence of the original cast structure has not entirely disappeared.

Since these specimens were obtained from a tensile test bar cast and annealed in the same manner as those used in the tensile tests, it is probable that the structure of all tensile bars just previous to test consisted of large grains typical of a cast structure in which a large number of small grains had appeared, the number and size of the latter increasing with the temperature of test.

In order to test the assumption that the recrystallization was due to annealing after strain, zinc free from strain was obtained by allowing a quantity of molten metal to freeze and cool very slowly

<sup>13</sup> A. Sauveur. The Metallography and Heat Treatment of Iron and Steel, 2d ed., pp. 265-271, 1916.

in a crucible. A specimen (No. 30) was then cut from this unstrained zinc, polished, etched, then repolished and etched several times in order to remove any strained surface that may have been produced

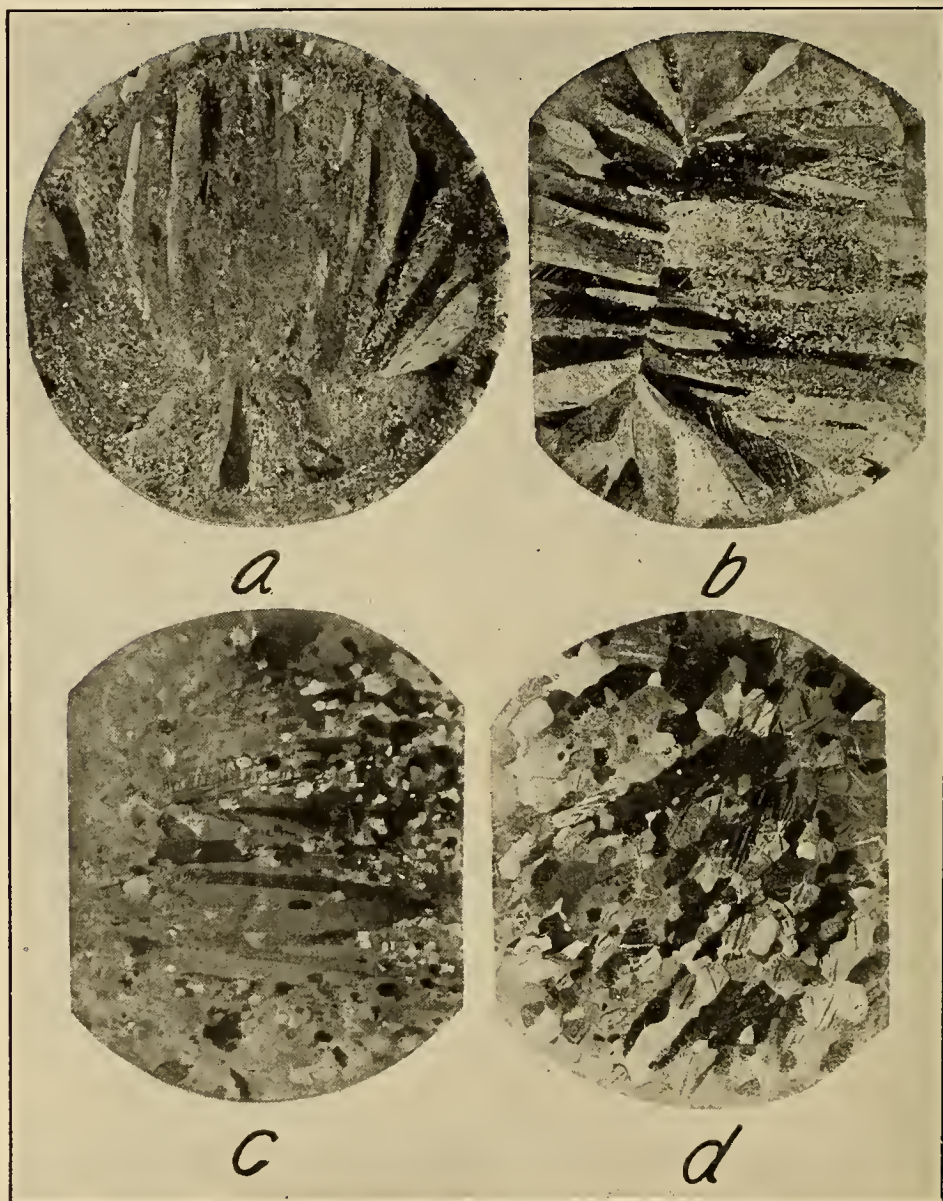


FIG. 5.—Structure of tensile test bar before test

- a. Specimen 20, annealed at 150° C.
- b. Specimen 7, quenched from 154° C.
- c. Specimen 12, quenched from 267° C.
- d. Specimen 19, quenched from 342° C.

Etching reagent: 5 per cent alcoholic hydrochloric acid.  $\times 3$ .

during operations preceding the final polishing. The structure is shown in Figure 6 (a). This specimen was then heated in an oil bath at 125, 150, and 220° C., respectively, for one hour, cooled slowly in the bath, and etched after each heating. There was no

evidence of the formation of new grains. The specimen was then heated to 390° C. in air and slowly cooled in the furnace, polished just sufficiently to remove all traces of the previous structure, and reetched (fig. 6 (b)). The difference noted is believed to be due to

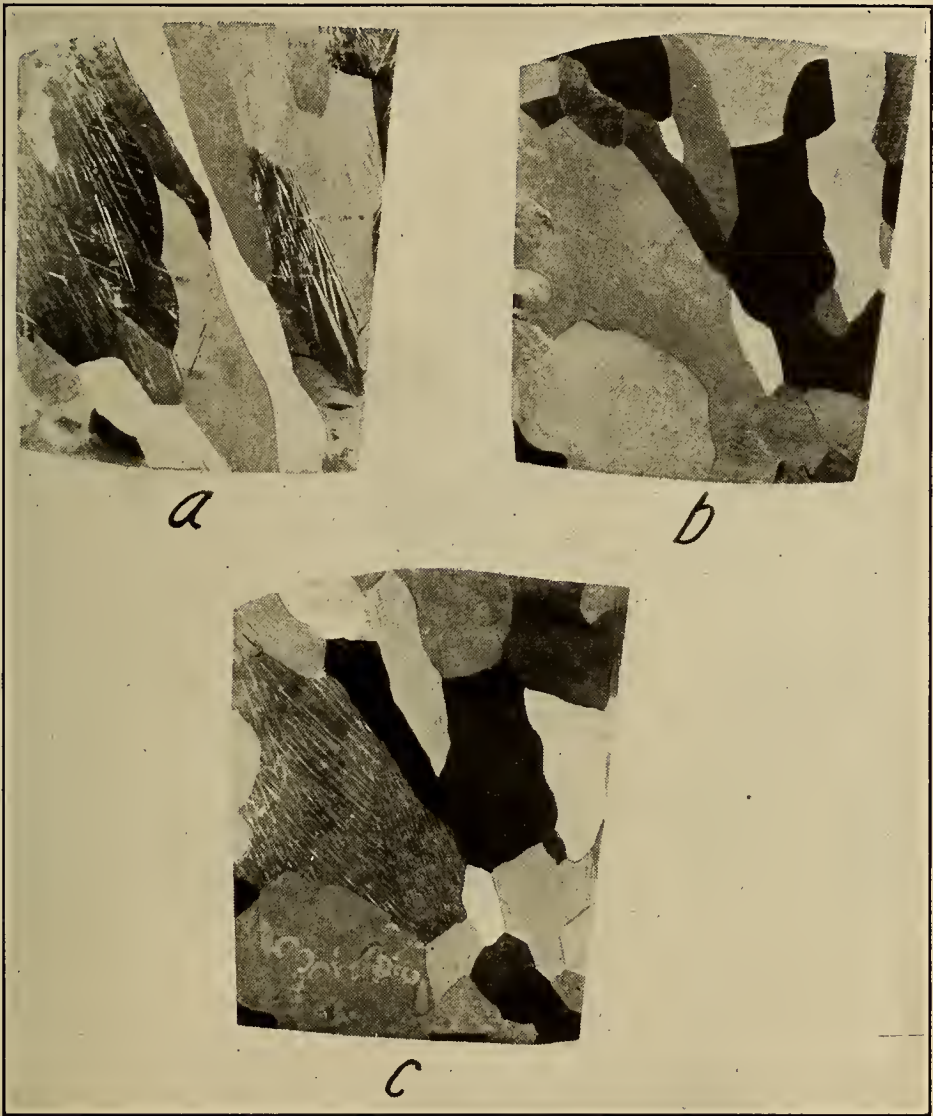


FIG. 6.—Specimens of strain-free zinc after various heat treatments

- a. Specimen 30, slowly cooled in the crucible from above the melting point, annealed at 125, 150, and 220° C. for one hour.
- b. Same specimen after annealing at 390° C. for one hour and slight repolishing.
- c. Same specimen after annealing at 390° C. in hydrogen for one hour very slightly repolished and etched.

Etching reagent: 5 per cent alcoholic hydrochloric acid. X3.

the removal of a thin layer of metal during polishing. Portions of grains visible in Figure 6 (a) may be seen in Figure 6 (b). In order to obtain further evidence on this point, the same specimen was annealed again for one hour at 390° C., this time in an atmosphere

of hydrogen in order to preserve the etched surface. After reetching no new grains were found as is evident by comparing Figure 6 (b) and (c). The fact that strain-free zinc does not recrystallize when annealed at temperatures up to 390° C. is strong evidence that zinc has no allotropic transformations.

The fractures of tensile test specimens (Nos. 21, 26, and 31, fig. 7) were considered representative of the three characteristic types of fractures obtained. Longitudinal sections, copper plated to protect the edges during grinding and polishing operations, were prepared.

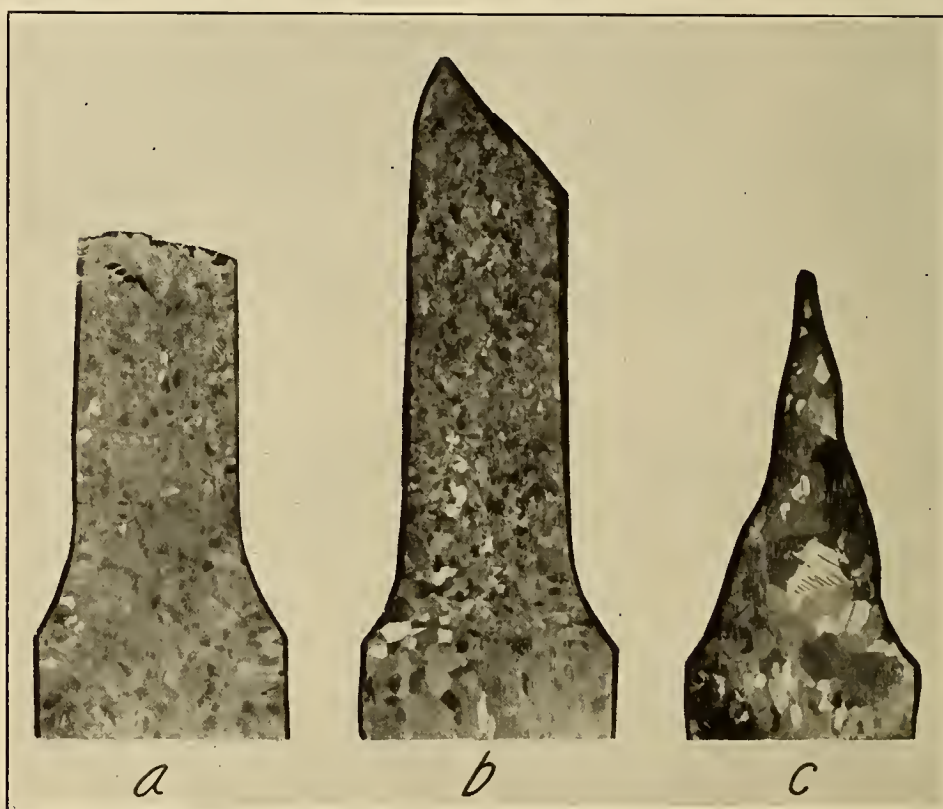


FIG. 7.—Macrostructure of longitudinal sections of three characteristic fractures obtained in tensile tests at elevated temperatures

a. Specimen 21, 62° C., "brittle" fracture.

b. Specimen 26, 200° C., "oblique" fracture.

c. Specimen 31, 350° C., "wedge" fracture.

Etching reagent: 5 per cent alcoholic hydrochloric acid.  $\times 2$ .

The macrostructures are shown in Figure 7 (a), (b), and (c). In each case the structure was relatively fine-grained as would be expected since the zinc was strained during the tensile test at the elevated temperatures and consequently recrystallized. In Figure 7 (b) the difference in grain size between the strained portion and unstrained portion at the shoulder of the specimen is evidence of this recrystallization. The grain size in the reduced section of specimen 31 (fig. 7 (c)) was noticeably greater than the others because of the higher temperature of test (350° C.). In this specimen it is apparent that

fracture has occurred through a single grain at the edge of the wedge. It is not believed, however, that a single crystal necessarily extended across the entire cross section of the tensile specimen at the time of fracture. The fracture was transcrySTALLINE in each case rather than intercrystalline as might be expected, especially at elevated temperatures. A similar result has been reported by Mathewson<sup>14</sup> in tensile tests of zinc up to 200° C.

(d) THEORETICAL CONSIDERATIONS.—It is known that pure zinc when severely cold-worked recrystallizes at normal atmospheric temperatures.<sup>15</sup> Mathewson<sup>16</sup> places the equicohesive temperature of a pure zinc in the neighborhood of 40° C. and in the same paper (p. 356) also states that complete recrystallization is found at 125° C. In general, complete recrystallization as shown by their work appears to occur between 75 and 125° C., according to the amount of cold work the zinc has received.

X-ray crystal analysis has shown that zinc crystallizes in the triangular close-packed system. Davey<sup>17</sup> points out from the work of Mark, Polanyi, and Schmid, and others that the planes of easiest slip in zinc are the 00.1 (basal) planes and that the planes of next easiest slip are the 10.0 planes. Mark<sup>18</sup> and his coworkers found that during a tensile test on a single crystal wire of zinc the planes of easiest slip (00.1) tended to rotate toward the axis of pull, thus accounting for the remarkable elongation values obtained.

In the tensile tests reported in the present work, as stated before, the structure just previous to test probably consisted of large grains typical of a cast metal in which had appeared a number of small grains typical of annealed material, the latter increasing in size with the temperature of test, and inasmuch as all specimens had been annealed at 150° C. previous to test, recrystallization was complete. The results obtained in the tensile tests might possibly be explained by the occurrence of an allotropic change, but the evidence from the thermal expansion, density, hardness, microscopic, and X-ray studies (see p. 690) does not support this theory. It is believed that the character of the tensile fractures obtained may be due to a preferred orientation of the crystals as discussed below.

In the mold used for casting the tensile test bars (fig. 2) it is evident that during cooling the reduced section of the casting is subjected to shrinkage stresses which cause a definite strain similar in effect to the straining of a tensile bar at an elevated temperature.

<sup>14</sup> Mathewson, Trewin, and Finkeldey, Some properties of and applications of rolled zinc strip and drawn zinc rod, *Trans. A. I. M. M. E.*, **64**, p. 334.

<sup>15</sup> Jeffries and Archer, *The Science of Metals*, p. 86.

<sup>16</sup> See p. 329 of publication cited in footnote 14.

<sup>17</sup> W. P. Davey, Application of X-ray crystal analysis to metallurgy, *Trans. A. S. S. T.*, p. 375; September, 1924.

<sup>18</sup> See footnote 7, p. 664.

The specimen was subsequently annealed at 150° C. This treatment is analogous to that first described by Carpenter and Elam<sup>19</sup> for the preparation of single crystals of aluminium.

Jeffries and Archer<sup>20</sup> state that in severe cold-rolling the crystal fragments in a metal tend to orient themselves in the same direction with the planes of easiest slip parallel to the direction of rolling, and the entire strip thus tends to acquire the properties of a single crystal.

It is evident from the foregoing consideration that in all tensile tests above normal atmospheric temperatures and particularly above 75° C. the zinc is being severely strained at temperatures at which spontaneous recrystallization is occurring during the entire period of the test. Since the zinc had previously been subjected to treatment tending to cause the formation of a single crystal, and severe cold work tends to produce a uniform orientation of the

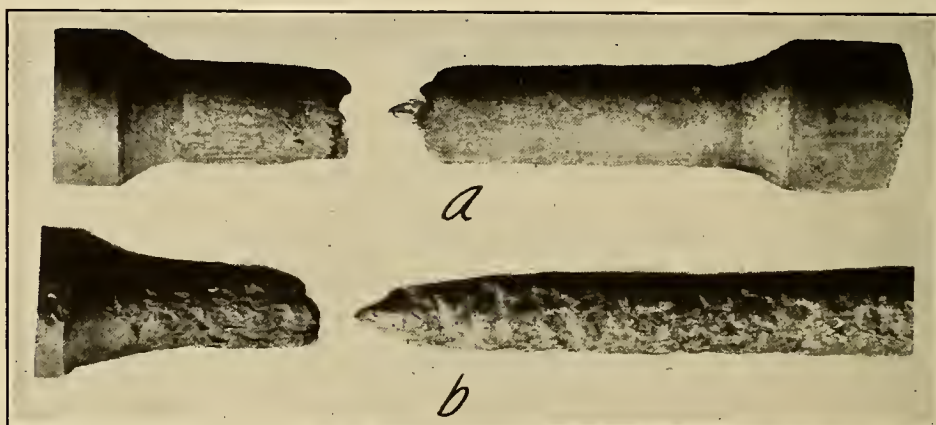


FIG. 8.—Influence of shrinkage strains on tensile fracture at 200° C.  $\times 1$

a. No shrinkage strains

b. Shrinkage strains present

crystals, a pronounced tendency for the new grains that are forming during strain at elevated temperatures to orient themselves in a uniform direction might be expected. Simultaneously a rotation of the crystals as obtained in single crystals<sup>21</sup> during cold work may occur

The result of these very complex changes would be then to produce during the tensile test a polycrystalline structure in which the 00.1 planes of the triangular close-packed lattice tend to rotate toward the direction of stress. The fracture obtained would consequently be of the single crystal type. The temperature of test and rate of application of stress would undoubtedly have an important influence on the results obtained.

<sup>19</sup> Carpenter and Elam, The production of single crystals of aluminum and their tensile properties Proc. Royal Soc., **100**, p. 329; 1921-22.

<sup>20</sup> Jeffries and Archer, The Science of Metals, p. 206.

<sup>21</sup> See footnote 7 p. 664.



In order to determine whether the shrinkage strains set up during cooling of the specimen in the mold had an important influence on the results obtained, the strains were practically eliminated by machining out the mold (fig. 2) to a uniform diameter of 1 inch. Tensile tests were then made on specimens machined from these comparatively strain-free bars in the same manner as previously described. A fractured specimen (No. 37) cast in this manner and tested at 200° C. is shown in Figure 8 (a). It is evident that the fracture is of the "brittle" type and not of the "oblique" type previously obtained at this temperature. As a further confirmation of this influence of shrinkage strains, the reduced section was replaced in the mold by means of metal liners and another specimen (No. 40) cast. Its fracture is shown in Figure 8 (b). It is evident that the "oblique" type of fracture has been obtained again as a direct result of the reduced section in the mold.

The effect of the shrinkage strains, however, is only apparent at the lower temperatures as shown by the following tests: Specimen

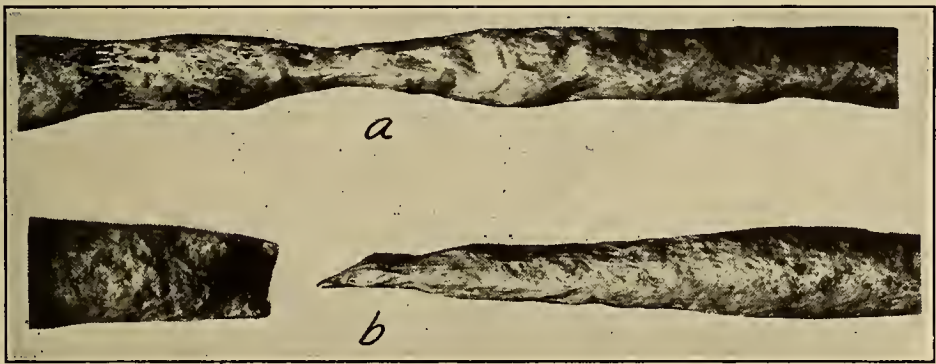


FIG. 9.—Influence of shrinkage strains on tensile fracture at 310° C.  $\times 1$

- a. No shrinkage strains  
b. Shrinkage strains present

No. 43 (fig. 9 (a)) was cast comparatively strain-free similar to specimen No. 37 (fig. 8 (a)) while specimen No. 44 (fig. 9 (b)) was cast with liners replaced similar to specimen No. 40 (fig. 8 (b)). Unfortunately during test of specimen No. 43 the heating bath caught fire and test could not be completed to fracture. The specimen showed, however, that the fracture would have been of the wedge type, as is apparent in Figure 9 (a).

The conclusion may be drawn that the influence of the shrinkage strains on the type of tensile fracture is of importance only at the lower temperatures.

(e) X-RAY STUDIES OF TENSILE FRACTURES.—An attempt was made by means of X-ray crystal analysis to determine the validity of the hypothesis of preferential orientation stated above. Apparatus ordinarily used for determining crystal orientation was not available, but by making certain assumptions it was thought that the

apparatus used for determining the crystal structure described later (see p. 686) in this report could be used.

It was assumed that if the crystals in a given tensile specimen had other than random orientation this fact would be indicated by a change in the number and intensity of bands in the diffraction pattern, and, further, that if the three specimens were placed in the same relative position with respect to the incident X-ray beam, any tendency toward uniform orientation of crystals would be registered in the diffraction patterns. The angle of orientation of the crystals in a given specimen could then be computed.

The mates to the three fractures shown in Figure 7 (specimen Nos. 21, 26, and 31) were used. The respective positions of the specimens relative to the incident X-ray beam are indicated in Figure 10.

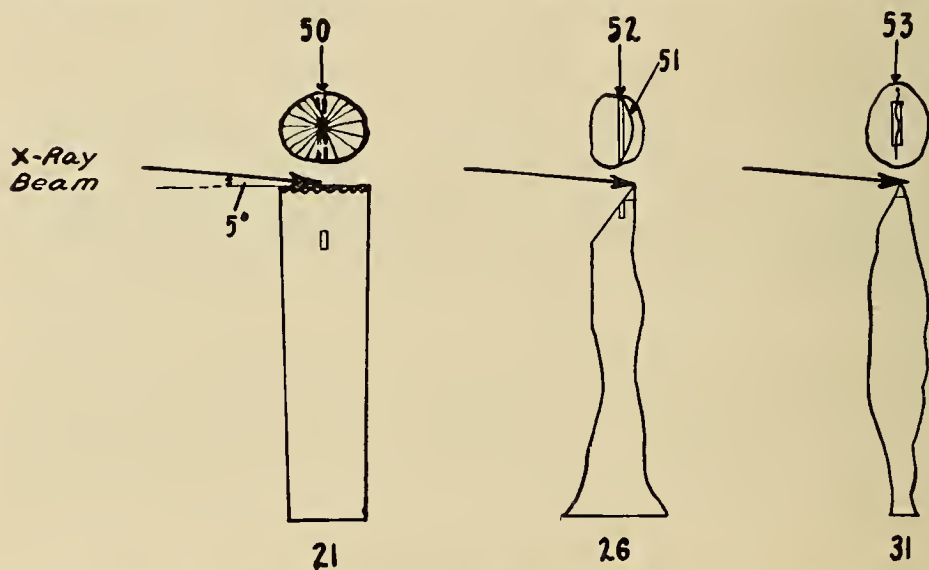


FIG. 10.—Relation between specimens and incident X-ray beam

As it was impossible to place the entire specimen in the apparatus, small specimens were cut out and mounted in the same relative positions as shown in the diagrams (fig. 10). The numbers appearing in the diagram will hereinafter be used in referring to the specimens. All specimens were exposed simultaneously for 32½ hours.

Results of measurement of the diffraction patterns are given in Table 7. The band of greatest intensity in each of the photographs was far more intense than the others and more intense than in the pattern of powdered zinc. The missing bands may be considered for the present to have zero intensity. Thus, in specimen 51 two intense bands appeared and all the rest were of zero intensity. Such a redistribution of intensity signifies that the crystals are oriented in such a way that "reflection" occurs only among a limited number of crystal planes. This may occur (1) when the crystals are large, and (2) when the crystals are oriented in the same direction. This second

condition is similar to that in a single crystal. In the present specimens the redistribution of intensity is thought to be due chiefly to the second cause, although the first is probably contributory as evidenced by the dashed pattern. Thus, in the pattern of specimen 51, which broke at an angle of about 35° with the longitudinal axis, the two bands recorded on the film represent the 10.1 planes and the 10.0 planes, the 10.1 reflection being the more intense. Hence, it is concluded that in this specimen the majority of the crystals are oriented so that the 10.1 planes are in a position to reflect the beam of X rays.

TABLE 7.—Bands observed in diffraction patterns of tensile specimens

Indexes of planes	Planar spacings				
	Powdered Zn	Specimen 50, brittle fracture	Specimen 52, oblique fracture	Specimen 51, oblique fracture at tip	Specimen 53, wedge fracture at tip
00.1 (2) .....	2.46	<i>2.46</i>	.....	.....	2.43
10.0 .....	2.295	2.28	2.29	2.28	2.28
10.1 .....	<i>2.070</i>	2.07	<i>2.07</i>	<i>2.07</i>	<i>2.09</i>
10.2 .....	1.673	1.67	.....	.....	.....
10.3 .....	.....	.....	.....	.....	.....
11.0 .....	1.325	.....	1.323	.....	1.318
00.1 (4) .....	1.252	.....	.....	.....	.....
11.2 .....	1.164	1.161	.....	.....	1.161
10.0 (2) .....	1.148	.....	.....	.....	.....
20.1 .....	1.114	.....	1.100	.....	1.112
10.4 .....	1.085	.....	1.077	.....	.....
10.1 (2) .....	1.039	.....	.....	.....	.....
20.3 .....	.939	.....	.....	.....	.938
10.5 .....	.905	.900	.898	.....	.....
11.4 .....	.....	.....	.....	.....	.....
12.0 .....	.....	.....	.....	.....	.....
12.1 .....	.854	.....	.....	.....	.850
10.2 (2) .....	.835	.....	.834	.....	.....
00.1 (6) .....	.820	.....	.....	.....	.....
12.2 .....	.....	.....	.....	.....	.....
10.6 .....	.....	.....	.....	.....	.....
12.3 .....	.770	.765	.769	.....	.....
10.0 (3) .....	.....	.....	.....	.....	.....
20.5 .....	.....	.....	.....	.....	.....
30.2 .....	.731	.729	.....	.....	.....

The most intense band in each case is shown by italic figures.

It is possible to compute the angle that any family of planes makes with the incident beam by means of the fundamental equation,

$$n\lambda = 2d \sin \theta$$

Then the angle made by other planes, such as the 00.1 (basal) planes, with the incident beam may be calculated, and finally the angle made by the basal planes and the longitudinal axis of the specimen. The last fact is the important one to know in this case as these planes have the highest atomic population and according to theory and experiment<sup>22</sup> are the planes of the easiest slip.

<sup>22</sup> See footnote 7, p. 664

The computations for specimen 51<sup>23</sup> (the tip of the "oblique" fracture) are as follows:

To determine the angle  $\theta$  (fig. 11) between the 10.1 plane and the incident X-ray beam:

$$n \lambda = 2d \sin \theta \quad (1)$$

$n$  = order of reflection = 1.

$\lambda$  = wave length of X rays = 0.710 Å (average, 0.708 and 0.712)

$d_{10.1}$  = distance between 10.1 planes = 2.08 (approximate, theoretical)

$\theta$  = angle between incident beam and 10.1 planes.

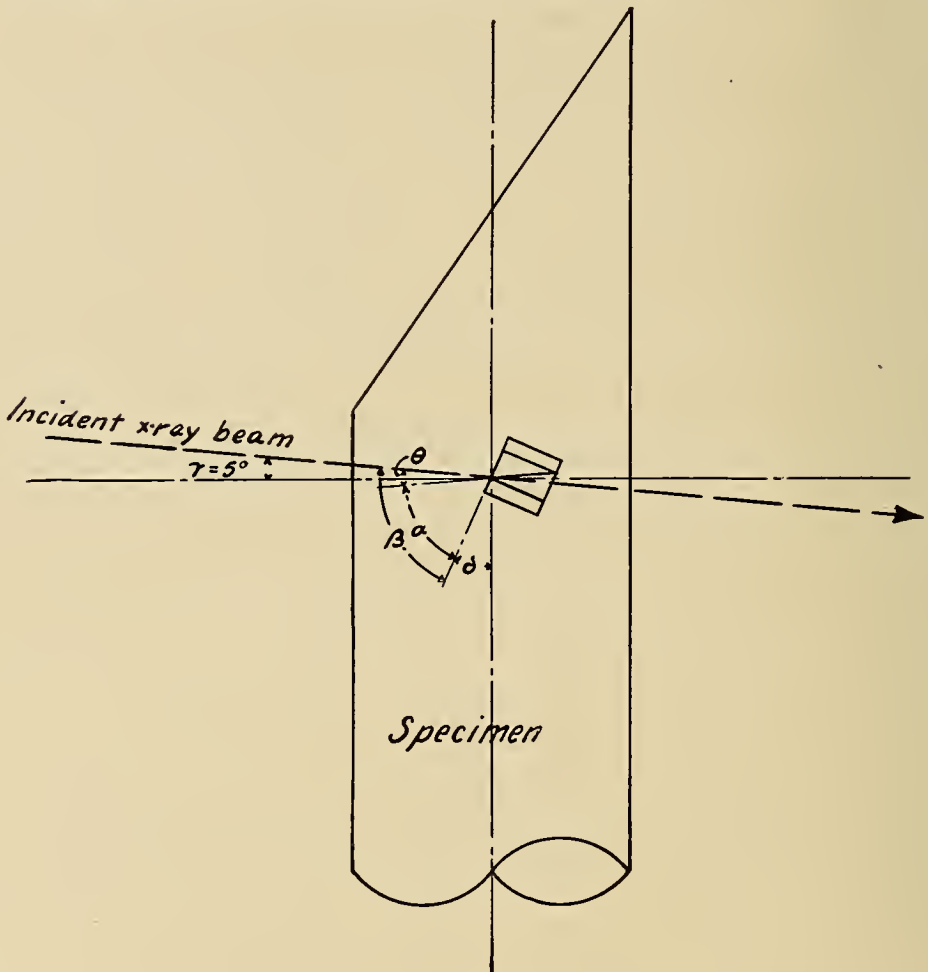


FIG. 11

Rewriting equation 1 to solve for  $\theta$ :

$$\sin \theta = \frac{n \lambda}{2d_{10.1}}$$

$$\sin \theta = \frac{1 \times 0.710}{2 \times 2.080} = \frac{0.170}{4.160} = 0.1706$$

$$\theta = 9^\circ 49'.3$$

<sup>23</sup> These computations apply also to specimens 52 and 53, in which the 10.1 planes were the principal ones recorded.

To determine the angle  $\alpha$  (fig. 12) between the 00.1 (basal) plane and the 10.1 plane:

$$\tan \alpha = \frac{c_0}{d_{10,0}} = \frac{4.929}{2.295} = 2.1477$$

$$\alpha = 65^\circ 2'.0$$

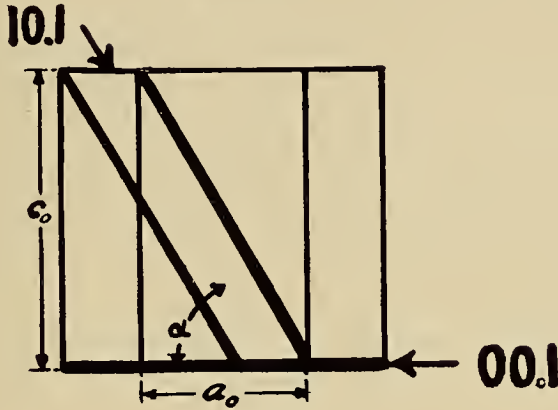


FIG. 12

To determine the angle  $\beta$  (fig. 11) between the 00.1 (basal) plane and the incident beam:

$$\beta = \theta + \alpha$$

$$\beta = 9^\circ 49'.3 + 65^\circ 2'.0$$

$$\beta = 74^\circ 51'.3$$

To determine the angle  $\delta$  (fig. 11) between the 00.1 (basal) plane and the longitudinal axis of the specimen.

$$\delta = 90^\circ - \beta + \gamma$$

$$\delta = 90^\circ - 74^\circ 51'.3 + 5^\circ$$

$$\delta = 20^\circ 8'.7$$

The computations for the brittle fracture are as follows:

$$\sin \theta = \frac{n\lambda}{2d}$$

$$n = 2$$

$$d_{00.1(2)} = 2.465$$

$$d_{00.1} = 2.465 \times 2 = 4.930$$

$$\sin \theta = \frac{2 \times 0.710}{2 \times 4.930} = 0.1440$$

$$\theta = 8^\circ 16'.8$$

$$\theta = \alpha$$

$$\beta = \alpha$$

$$\delta = 90^\circ - \beta + \gamma$$

$$\delta = 90^\circ - 8^\circ 16'.8 + 5^\circ$$

$$\delta = 86^\circ 43'.2$$

Films of specimens 51 and 53 turned  $180^\circ$  on their axes gave results which agreed with the foregoing considerations.

The relative order of the 00.1 (basal) planes, angle of fracture, and angle of maximum shear to the axis of the specimen is indicated in Figure 13 *a* and *b*, respectively, for a specimen tested close to normal temperatures and one at an elevated temperature. In Figure 13(*a*) only a slight majority of the basal planes are supposed to be oriented in the direction indicated, the remainder having random orientation. In Figure 13(*b*) a much larger number of these planes is represented.

In the diffraction pattern of the brittle ( $90^\circ$ ) fracture the most intense band corresponds to the 00.1 plane (this band is relatively more intense than normally), thus indicating that slightly more of the crystals were oriented in the direction shown in Figure 13(*a*) than

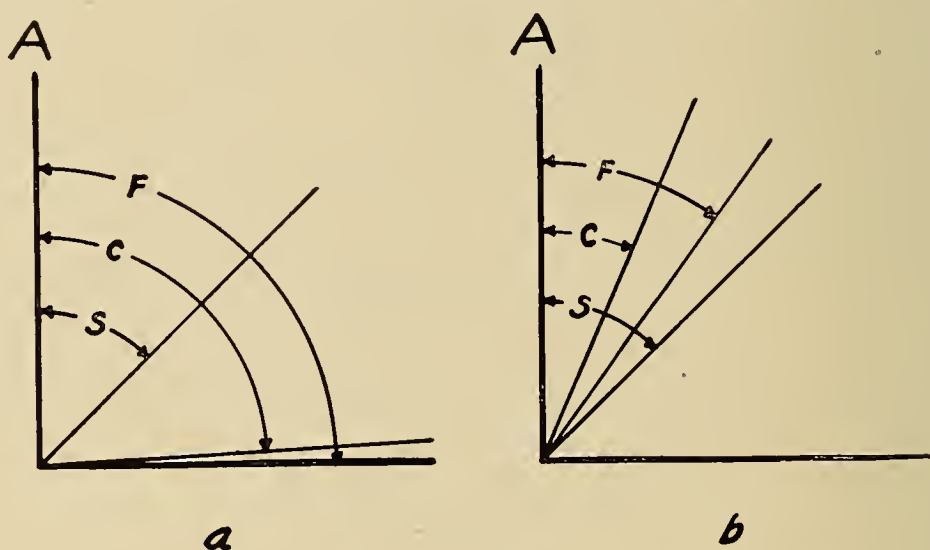


FIG. 13.—Comparison of angle of “brittle” (*a*) and “oblique” (*b*) fractures

S=angle of maximum shearing stress

C=orientation of a slight majority of basal planes in *a* and of a majority in *b*.

F=angle of fracture

would be expected in truly random orientation. If this be true, a slight tendency toward preferred orientation exists when the metal is stressed (as in a tensile test) at  $60^\circ$  C. In the specimens with “oblique” and “wedge” fractures computation indicates the majority of the 00.1 (basal) planes to be at an angle with the axis of pull considerably less than the angle of maximum shear stress. The orientation of the crystals in the “wedge” fracture (No. 53) appears to be somewhat more random than in the “oblique” fracture. This may be due to the greater length of time required in cooling the specimen from the higher temperature, with the consequently greater opportunity for recrystallization into a random orientation after fracture.

The X-ray data given indicate that the hypothesis of a preferred orientation is a plausible one in that a majority of the 00.1 (basal) planes probably tend toward an angle with the direction of applied stress.

After the X-ray studies described above were completed a paper<sup>24</sup> came to the attention of the authors in which studies were reported of the thermoelectric effect in single crystal wires made by the method of Czochralski. In this method the wires are drawn from a bath of molten zinc through a hole in a mica disk. It was stated that by suitable regulation of the speed with which the crystal was drawn from the melt the desired orientation could be produced. At the beginning of growth the angle between the longitudinal axis of the wire and the hexagonal axis of the crystal was 90°. As the crystal was withdrawn from the liquid the angle decreased progressively, reaching 45° at 25 cm. It is quite probable that the stress due to the weight of the growing crystal produced this rotation. It was stated that by amalgamating the crystals with mercury they became brittle and could be split along the basal plane with a knife.

The fractured end of one of the present tensile specimens of the wedge type (specimen 10 at 288° C.) was treated with mercury for several hours. At the end of this time it was found possible to split off several sections from the face of the fracture. The faces revealed were at a steep angle with the longitudinal axis of the specimen. The specimen was treated some time longer and then squeezed in the jaws of a vise. Crystal fragments cleaved off easily. The general direction of the cleavage faces was between 45 and 0° with the longitudinal axis. This condition is shown in Figure 14. A specimen broken in tension at 18° C. was treated with mercury, but it was more difficult to split sections from the crystals. When gripped in a vise and broken, however, the crystals were seen to be oriented in the manner of a cast material, the cleavage faces radiating from the center and diversely oriented with respect to the longitudinal axis. The cleavage faces did not approach the angles exhibited by the former in any case. The evidence given here further substantiates the hypothesis of crystal reorientation at elevated temperatures.



FIG. 14. — Orientation of cleavage faces in specimen 10 tested at 288° C.

Crystal fragments were split from the fracture after amalgamating with mercury.  $\times 1\frac{1}{2}$

<sup>24</sup> E. G. Linder, Thermoelectric effect in single crystal zinc wires, *Phys. Rev.*, **26**, p. 486; October, 1925.

## PART II

## I. CRYSTAL STRUCTURE

## 1. METHOD

X-ray diffraction patterns of zinc in the form of powder, and ribbon were obtained by the well-known "powder" method.<sup>1,2</sup> A commercial X-ray diffraction apparatus<sup>3</sup> equipped with a Coolidge tube with water-cooled anode was used. In this type of apparatus the X rays, which originate from a molybdenum target, are filtered through a zirconium oxide filter. The diffraction pattern is produced by the molybdenum  $K_{\alpha}$  doublet.

The specimens were made of the same material as those used in the preceding experiments. The powder, obtained by vacuum distillation, was also furnished by the New Jersey Zinc Co. The ribbon used in the work at elevated temperatures described later was made by rolling wire drawn from cast rods. The specimens were mounted in thin-walled pyrex glass tubes.

In order to correct the readings for errors introduced by small changes in dimension of the film and the locating of the undeviated or "zero" image, the powder specimens were run with comparison standards of sodium chloride for which reliable X-ray data are to be had. The salt used was obtained from the "chemically pure" substance by two crystallizations in hydrochloric acid and ignition to 675° C. One half of the specimen tube contained the zinc powder and the other half the pure salt, which had been sifted through 200-mesh bolting cloth. The two substances were separated by cotton and the reflected rays by a metal septum in the "cassette" or film holder. Thus, the pattern of the zinc and that of the standard substance were recorded on opposite halves of the same film

## 2. RESULTS

By using a calibrated scale furnished with the apparatus, the spacings in Ångström units between the various crystallographic planes of the zinc lattice were read directly from the spacings of the bands in the diffraction pattern. By means of charts<sup>4</sup> on which are given the calculated relative planar spacings and corresponding axial ratios for a number of different crystal systems, the type of lattice, axial ratio, and indexes of planes giving rise to the different bands on the film were determined.

<sup>1</sup> P. Debye and P. Scherrer. Interference of X rays using irregularly oriented substances, *Physikal. Z.*, **17**, p. 277; 1916.

<sup>2</sup> A. W. Hull. A new method of X-ray crystal analysis, *Phys. Rev.*, **10**, p. 661; 1917.

<sup>3</sup> W. P. Davey. A new X-ray diffraction apparatus, *Jour. Opt. Soc. Am.*, **5**, p. 479; 1921.

<sup>4</sup> A. W. Hull, and W. P. Davey, Graphical determination of hexagonal and tetragonal crystal structures from X-ray data, *Phys. Rev.* **17**, p. 549; 1921.



Measurements on the film in each case were made from the center of the shadow of the specimen, produced by the undeviated X rays, to the centers of the bands of the diffraction pattern. These values were corrected for errors, such as those previously mentioned, as follows: The experimentally determined values for the planar spacings of the sodium chloride crystal were plotted against the established values for this salt and a curve drawn which gave the deviation in Ångstrom units of the observed values from the true values. Corrections for the zinc spacings at any point on the film were obtained from this curve.

The corrected results for a film of powdered zinc at normal temperatures are summarized in Table 8. Column 1 gives the Miller indexes of the crystallographic planes as read from the chart of the triangular close-packed lattice at an axial ratio of 1.86 (the ratio of the length of a side of the base of an elementary prism to the altitude of the prism). Column 2 gives the spacings of the planes in Ångstrom units divided by the order of reflection. Column 3 gives the intensities of the bands estimated on a scale of 10. Column 4 gives the values in Ångstrom units for  $a_0$ , the length of a side of the base of a unit cell, calculated from the observed planar spacings. These values were obtained by dividing the observed planar spacings by the corresponding relative spacings calculated for a triangular close-packed lattice of axial ratio 1.86. The length of time of exposure was 38 hours at 20 milliamperes.

TABLE 8.—Typical data from a diffraction pattern of powdered zinc (film 1)

Indexes of planes	$d_{hkl}/n$	Intensity <sup>1</sup>	$a_0$
00.1 (2)-----	2.465 A	3	2.650 A
10.0-----	2.300	2	2.656
10.1-----	2.080	10	2.649
10.2-----	1.680	1½	2.651
10.3-----	1.334	3	2.646
11.0-----	1.325	3	2.650
00.1 (4)-----	1.232	½	2.649
11.2-----	1.164	3½	2.643
10.0 (2)-----	1.148	¼	2.651
20.1-----	1.116	3½	2.646
10.4-----	1.085	⅛	2.648
10.1 (2)-----	1.040	⅛	2.649
20.3-----	.939	¼	2.645
10.5-----	.905	½	2.648
11.4-----			2.658
12.0-----			
12.1-----	.854	¾	2.650
10.2 (2)-----	.838	⅛	2.644
00.1 (6)-----	.820	⅛	2.645
12.2-----			2.655
10.6-----			
12.3-----	.766	¼	2.646
10.0 (3)-----			2.653
20.5-----			
30.2-----	.730	⅓	2.649
Average-----			2.649

<sup>1</sup> Estimated on a scale of 10, this figure corresponding to the darkest band.

Hull's result that zinc crystallizes in the hexagonal (triangular) close-packed system was confirmed. Table 9 summarizes the results of measurement of three powder films of zinc, the average value for  $a_0$  being 2.65 Å. It will be noted that the result given here is at variance with the value of 2.670 Å generally quoted in the literature, based on Hull's work. Doctor Hull, in private communication, confirmed the value of 2.65 as the correct one. His calculated values for the first 12 planar spacings, arranged in decreasing order of magnitude, agree very closely with those calculated by means of the set of factors used in the present work, the average deviation being only 0.0008 Å. Below the 1.040 Å spacing, however, a nearly constant difference of 0.006 Å occurs. If the present factors for this range of spacings are applied to the value 2.67 Å instead of 2.65 Å the theoretical planar spacings given by Hull are obtained. It is supposed that this is where the discrepancy arose.

TABLE 9.—Summary of results of values for  $a_0$ .

Film	$a_0$
1-----	2.649
2-----	2.649
3-----	2.650
Average...	2.649=2.65

The diagram of the unit cell<sup>29</sup> of zinc with dimensions as determined from the present X-ray data is shown in Figure 15. The points at which atoms are located are represented by black spheres.

### 3. DENSITY FROM X-RAY DATA

When data on the crystal structure of a substance are available, as in the present case, the density ( $\rho$ ) may be calculated<sup>5</sup> by means of the expression

$$\rho = \frac{mM}{V} \quad (1)$$

where, for an elementary substance,  $m$  is the number of atoms included within the unit cell;  $M$  is the mass of the atom in grams (equal to the product of the atomic weight and the mass of one unit of atomic weight given by the value of  $1.649 \times 10^{-24}$  grams); and  $V$  is the volume of the unit cell in centimeters. The value of  $m$  is integral and may be determined from the geometry of the cell. This is apparent from inspection of Figure 15. At each of the four  $120^\circ$  intersections of the vertical faces one-sixth of an atom is contained within the cell; at each of the four  $60^\circ$  intersections, one-

<sup>5</sup> R. W. G. Wyckoff. The Structure of Crystals, p. 198. Chemical Catalog Co., New York.

twelfth of an atom; and 1 atom is contained entirely within the cell, making a total of 2 atoms. It is thought preferable to calculate the density on the basis of the unit cell shown, with its value of  $m=2$ , rather than on the basis of 1 atom per triangular prism as is sometimes done,<sup>6</sup> even though the result for  $\rho$  in either case reduces to the same quantity.

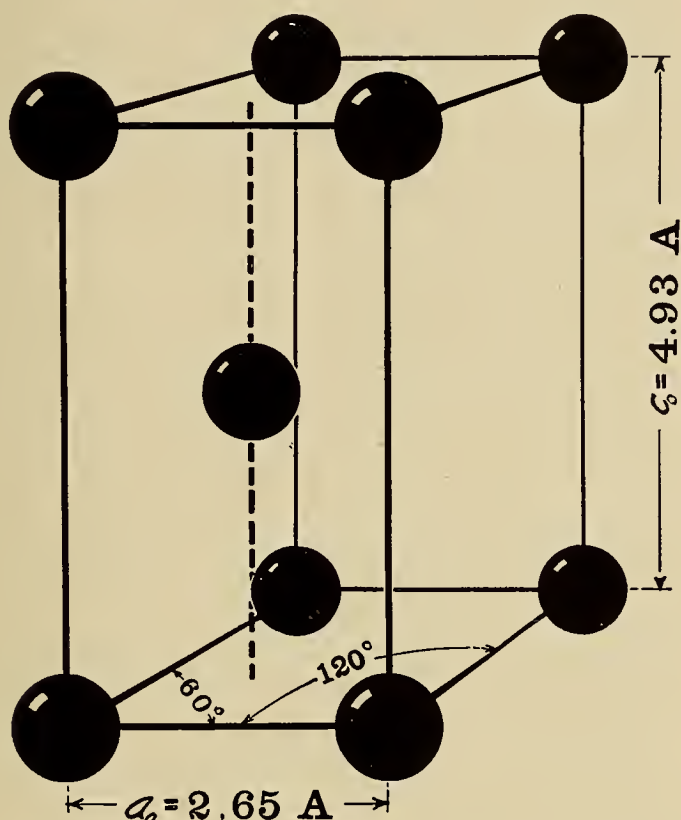


FIG. 15.—Unit cell of the triangular close packed zinc lattice with dimensions as determined from the present X-ray data  
The black spheres represent points at which atoms are located

The density calculated from equation (1) is therefore

$$\rho = \frac{mM}{a_0^2 c_0 \sin 60^\circ} = \frac{2 \times 65.38 \times 1.649 \times 10^{-24}}{(2.65 \times 10^{-8})^2 \times 4.93 \times 10^{-8} \times 0.866} = 7.19$$

It will be remembered that the density of cast zinc to the same number of significant figures when determined by the gravimetric method was 7.13. While any error in the constant  $a_0$  obtained by X-ray methods is cubed ( $V = a_0^2 \times a_0 \times c \times \sin 60^\circ$ ) in computing the density, it is not considered desirable at the present time to bring the value of  $a_0$  into accord with the value required by the density of the cast metal as determined in the usual manner. The two results, however, present an interesting comparison. The

<sup>6</sup> A. W. Hull. X-Ray crystal analysis of thirteen common metals, Phys. Rev., 17, p. 571; 1921.

value for the density calculated from the X-ray data of Peirce <sup>7</sup> is 7.127 and his experimentally determined values,<sup>8</sup> as stated earlier in this paper, were 7.150 to 7.135.

Wyckoff <sup>9</sup> states that for the reasons mentioned previously “ \* \* \* diffraction methods of obtaining densities are inherently inaccurate \* \* \*. The usefulness of X-ray methods for establishing densities seems to lie essentially in the fact that the moderately accurate determinations which are immediate by-products of crystal structure studies can be used to replace many of the very approximate data that now exist.” Another possible error, other than one resulting from the measurement of planar spacings, may arise from the determination of the axial ratio from the charts where the effect of a variation in the fourth significant figure is appreciable.

#### 4. X-RAY STUDIES AT ELEVATED TEMPERATURES

In order to examine, from the point of view of crystal structure, the claim that zinc exists in more than one allotropic form, X-ray diffraction patterns were obtained of specimens heated to temperatures between the points where the allotropic changes were supposed to occur.<sup>10</sup>

The specimens in the form of ribbons, prepared as described previously, were heated by their electrical resistance. The heating device attached to a cassette is shown in Figure 16. Connections to the source of current, consisting at first of storage batteries, but later of 10-volt alternating current because of the frequent battery replacement necessitated by the long exposures, were made through brass holders at each end of the zinc ribbon. The specimen and holders were insulated from the rest of the apparatus by a pyrex glass container. The dimensions of the whole device were such that the specimen retained its proper position with respect to the rest of the apparatus when the cassette was put into place. Consequently the linear distances and angles which are constants of the apparatus were substantially the same as usual and their redetermination was rendered unnecessary for this purpose. A stopcock was affixed for evacuating the tube, but this expedient was not found necessary in the present work.

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<sup>7</sup> W. M. Peirce, E. A. Anderson, and P. Van Dyck. An investigation of the alleged allotropy of zinc by X-ray analysis and a redetermination of the zinc lattice, *Jour. Frank. Inst.*, **200**, p. 349; 1925.

<sup>8</sup> See footnote 1, p. 662 (Peirce's discussion).

<sup>9</sup> See footnote 29, p. 688.

<sup>10</sup> Similar experiments were in progress at the New Jersey Zinc Co. After consultation, however, it was mutually agreed that independent investigation of this question was desirable.



FIG. 16.—Cassette with device for heating specimens  
run at elevated temperatures

- A. Cassette
- B. Specimen of zinc ribbon
- C. Brass holders for connection of specimen to source of current
- D. Specimen holder of pyrex glass

The various temperatures used were determined indirectly for ribbons of given dimensions from a temperature-current curve obtained by plotting the currents required to bring just to boiling a series of liquids of known boiling points. The experimental data are given in Table 10. The boiling point in each case was taken as

TABLE 10.—*Temperature-current calibration data for ribbon*

Substance	Boiling point	Current
	° C.	Amperes
Acetone.....	57	3.5
Alcohol.....	78.3	4.0
Water.....	100	4.3
Glycerin.....	291	6.1
Zinc.....	1 419.4	7.2

Melting point (B. S. Circular 35, 4th ed.).

the lowest current value which would just produce a hissing sound when the hot ribbon was dipped in a small quantity of the liquid. The curve is given in Figure 17. The uppermost point was taken as the current required to cause fusion of the zinc ribbon at a single point. The dimensions of the specimens used in the runs were the same as those used in the temperature determinations. At the completion of the runs these specimens were heated to melting and the currents required to accomplish this noted as a check on the temperature of the run. The temperatures of the two alleged allotropic transformations and the temperatures at which diffraction patterns were obtained are shown on the curve. All ribbons were annealed electrically before the runs.

The results are summarized in Table 11. Column 1 gives the indexes of the planes; column 2, the probable planar spacings at ordinary temperatures; columns 3, 4, and 5, the average observed values at the temperatures noted.

The lengths of time of exposure ranged from 40 to 70 hours at about 20 milliamperes. At elevated temperatures crystal growth occurs in the worked metal. Consequently, a pattern consisting of continuous bands, such as is produced by a substance composed of small and diversely oriented crystals, was replaced by the "dashed" pattern of a coarsely crystalline substance in which some bands are entirely outside the limits of the film. The explanation of this phenomenon is familiar to investigators of crystal structure. If a number of patterns are obtained from different specimens under similar conditions the total number of bands more nearly approaches the theoretical number, for some bands not appearing on one film

may appear on another. The fact that the general character of such a "composite" pattern and the values for the planar spacings are close to those produced by an ideal specimen is good evidence that the crystal structures represented by the two are the same.

From the results in Table 11 it is clear that no change in crystal structure has occurred at the elevated temperatures. The slight deviations in the values of the planar spacings given from those at normal temperatures may be attributed to the fact that the former

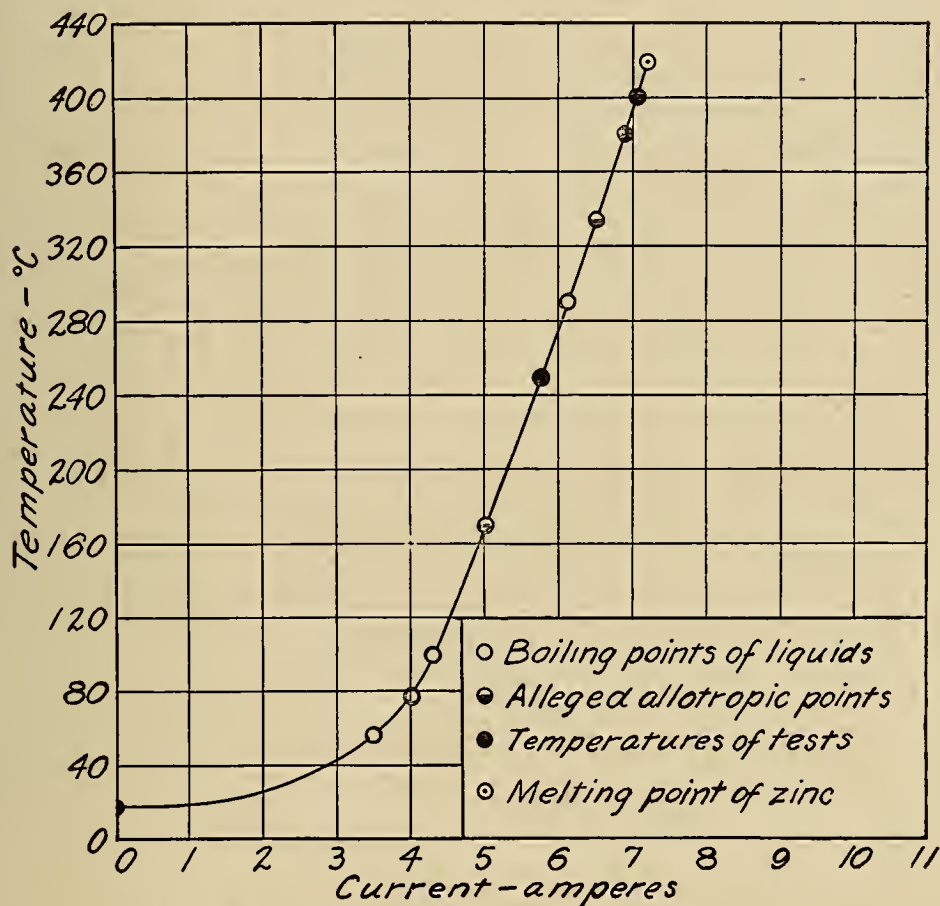


FIG. 17.—Temperature-current calibration curve for zinc ribbon

values were not corrected with a standard substance, the form of the specimens rendering this impracticable. Another error might easily be introduced by the irregularity in the position of the zero image of a specimen of twisted ribbon. Reflections from the edge of the portions in a vertical position would be in a slightly different position from those from an edge in the horizontal position. In view of these facts, the planar spacings in the group above 1.325Å which become inherently less accurate than the lower ones as their magnitude increases are not given to more than two decimal places.

TABLE 11.—Summary of results at elevated temperatures

Indexes of planes	$d_{hkl}/n$ probable at 20° C.	$d_{hkl}/n$ observed at elevated temperatures		
		250° C.	380° C.	400° C.
00.1 (2)-----	2.464A	2.46A		
10.0-----	2.295	2.30	2.28A	2.27A
10.1-----	2.080	2.07	2.09	2.07
10.2-----	1.679	1.67	1.68	1.69
10.3-----	1.336		1.34	1.35
11.0-----	1.325	1.325		
00.1 (4)-----	1.232	1.230		
11.2-----	1.167	1.162	1.165	1.169
10.0 (2)-----	1.147	1.147		1.147
20.1-----	1.118	1.112		1.118
10.4-----	1.086	1.080	1.087	
10.1 (2)-----	1.040	1.040	1.048	1.038
20.3-----	.941	.939	.945	
10.5-----	.906	.905	.908	
11.4-----	.902			
12.0-----	.867		.863	
12.1-----	.854	.853	.854	.854
10.2 (2)-----	.840	.830		
00.1 (6)-----	.822	.821		
12.2-----	.818			
10.6-----	.774	.775	.773	.779
12.3-----	.767	.763	.769	
10.0 (3)-----	.765			
20.5-----	.749			.747
30.2-----	.730	.731	.732	

It is therefore concluded from the results given above that no allotropy occurs in zinc if an allotropic change is considered to be accompanied by a change in crystal structure. This conclusion is in agreement with the results obtained by Peirce and his coworkers. The extra bands not required by the zinc lattice which were reported by these investigators to have appeared in patterns obtained at both normal and elevated temperatures were not found in films from the present work. Peculiar diffraction effects may arise from a number of causes, some of which have been described.<sup>11</sup>

## II. SUMMARY

A study has been made of some of the more generally determined physical properties of pure zinc (99.993 per cent), and also of the crystal structure by the X-ray diffraction method at normal and elevated temperatures. Together with these determinations, particular attention has been paid to the alleged allotropy of zinc.

Data are given on the following properties: Coefficient of expansion, density and scleroscope hardness of annealed and quenched material, Brinell hardness, and tensile properties and crystal structure at normal and elevated temperatures.

<sup>11</sup> R. M. Bozarth, An explanation of peculiar reflections observed on X-ray powder photographs, Jour. Opt. Soc. Am., 9, p. 123; 1924.



In the tensile tests an unusual type of fracture was obtained at elevated temperatures which is similar to fractures obtained in single crystals. A hypothesis is given to account for this unusual type of fracture.

### III. CONCLUSIONS

1. The average coefficient of linear expansion per degree centigrade of pure cast zinc over the temperature range 20 to 100° C. is 0.0000395 and over the temperature range 20 to 300° C. it is 0.0000393.

2. The density of pure cast zinc is 7.131 gms per cm<sup>3</sup>. There is no appreciable difference between the density of cast zinc as annealed or quenched from elevated temperatures up to 340° C.

3. The scleroscope hardness of pure cast zinc is not measurably affected by quenching the annealed material from elevated temperatures. The Brinell hardness of pure zinc decreases uniformly from approximately 31 at normal temperatures to 6.5 at 200° C.

4. The tensile strength of pure cast zinc is quite variable, but is probably about 4,000 lbs./in.<sup>2</sup> at normal temperatures. There are indications of a slight increase in the tensile strength at slightly elevated temperatures followed by a marked and consistent decrease beginning approximately at 100° C.

5. Microscopic studies of etched strain-free surfaces of cast specimens annealed at temperatures up to 390° C. give no evidence of recrystallization or grain growth.

6. The value for the length of side of an elementary prism of the triangular close packed lattice of zinc (axial ratio 1.86) at normal temperatures is 2.65A.

7. The density of zinc computed from the X-ray data is 7.19 g./cm<sup>3</sup>.

8. The crystal form at 250, 380, and 400° C. is the same as at normal temperatures.

9. The data obtained indicate that pure zinc has but one allotropic form.

The authors desire to express their appreciation of the continued interest and helpful suggestions of H. S. Rawdon throughout the progress of this work and the assistance of J. W. Brewer in preparation of specimens for microscopic examination

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