Light Figures of Zinc Crystals

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Synopsis

Light figures were observed on the three principal crystallographic planes {0001}, {11$\bar{2}$0} and {10$\bar{1}$0} of zinc crystals, which were etched for various time-intervals with variously concentrated aqueous solutions of various acids, alkalis, and salts. The suitability of observed figures for determining orientations of zinc crystals with the light-figure method was examined, and light figures obtained by etching for 20 minutes with boiling saturated aqueous solution of potassium hydroxide was found to be the most suitable for the perfect determination (the determination of all angles which the geometrically predominated axis of a crystal makes with the hexagonal axis and digonal axes of the first or second kind).

I. Introduction

The light figures of a metal crystal are light patterns produced by the reflection of a fine pencil of light on an etched surface of the crystal. The form of the light figures varies diversely with the lattice type of the crystal, the etching reagent and its temperature, and the time of etching. But the light figures show always the same symmetry characteristics as those of reflecting crystal planes, and this nature may be utilized for a rapid and accurate determination of crystal orientations(1). Previously, the senior of the present writers studied light figures of crystals of cubic metals—nickel, copper, iron, aluminium and face-centered nickel-iron alloys(2), and applied the method of light figures to the determination of orientations in the said metal crystals with great success(1).

Now, we have studied the light figures of hexagonal zinc crystals, especially with the aim of finding out figures suitable for determining crystal orientations. In a hexagonal crystal, the hexagonal axis, [0001], and the three digonal axes of the first kind,[2$\bar{1}\bar{1}$0], [$\bar{1}$2$\bar{1}$0]and[$\bar{1}\bar{1}$20,] four axes in all, are usually taken as the principal crystallographic axes (Fig. 1). Let a direction $\overrightarrow{OP}$ (Fig. 2) make an angle θ with the hexagonal axis

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(1) M. Yamamoto, Nippon Kinzoku Gakkai-shi (J. Japan Inst. Metals), **5** (1941), 214 (in Japanese); Sci. Rep. Tôhoku Imp. Univ., **31** (1943), 121.

(2) M. Yamamoto, Nippon Kinzoku Gakkai-shi, **4** (1940), 368 (in Japanese); Sci. Rep. Tôhoku Imp. Univ., **29** (1941), 113 (nickel and copper crystals); Nippon Kinzoku Gakkai-shi, **5** (1941), 324 (in Japanese) (iron and aluminium crystals); ibid., **6** (1942), 535 (in Japanese) (nickel crystals); Kagaku (Science), **14** (1944), 67 (in Japanese) (crystals of face-centered nickel-iron alloys).

and angles α, β and γ with digonal axes of the first kind, then the orientation of $\overrightarrow{OP}$ may be fixed by any two among those four angles. θ may be determined directly with a light figure produced by an (0001) plane, while α, β and γ directly with figures

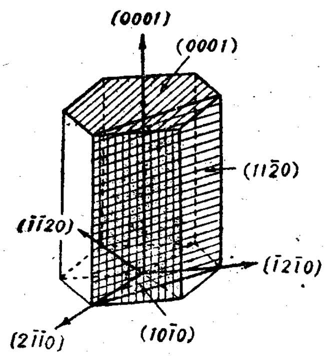

Fig. 1. Principal crystallographic axes and planes of a hexagonal crystal.

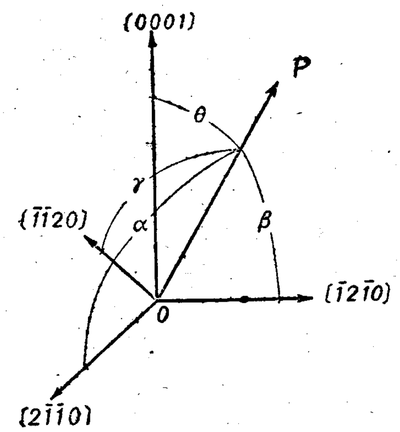

Fig. 2. Illustration of angles between the geometrical axis of a specimen crystal, $\overrightarrow{OP}$, and the four principal crystal axes of hexagonal crystal.

created by the three (11$\bar{2}$0) planes or indirectly with figures by the three (10$\bar{1}$0) planes.[3]

Thus, for a perfect determination of orientations of hexagonal crystals i.e. for the determination of θ as well as α, β and γ by the use of light figures, it is the first matter to know such directions of etching specimen crystals that produce distinct light figures, having a definite center of symmetry, on base planes and prism planes of the first or second kind.

II. Specimen Crystals and Experimental Procedures

Zinc crystals used as specimens are of a cylindrical-rod form, about 5mm in diameter and several cm in length. They were prepared by the Tammann-Bridgman method of the lowering-crucible type from three brands of zinc comprizing 98.83, 99.09 and 99.99% zinc[4]. For the study of light figures, however, it is not always necessary to use a perfect single crystal, but is sufficient to employ "imperfect" single crystals consisting of several coarse grains. A greater part of this work was performed with such specimens.

Reagents employed for etching zinc crystals are variously concentrated aqueous solutions of acids [(1) nitric acid, (2) hydrochloric acid, (3) *aqua regia*, (4) sulphuric acid, (5) hydrofluoric acid, (6) chromic acid anhydride and (7) mixture of nitric acid and chromic acid anhydride (94:6)] of alkalis [(8) sodium hydroxide and (9) potassium

(3) Actual application of the method of light figures to the determination of orientations of hexagonal crystals will be fully described in the succeeding report in this journal.

(4) Detail in the preparation of zinc single crystals by the Tammann-Bridgman method of the lowering-crucible type will be reported in the near future.

Table 1.

Experimental data on light figures of zinc crystals, etched with aqueous solutions of various acids, alkalis and salts. The mark ◎ denotes a distinct light figure, suitable to the determination of crystal orientations, ○ a distinct, but not so suitable, figure, △ a distinct, but unsuitable, figure and × an indistinct or no figure.

No.	Etching Reagent* (Temperature)	Sharpness and Suitability of Light Figure on $\{0001\}$	$\{11\bar{2}0\}$	$\{10\bar{1}0\}$	Optimum Etching Time	Form of Light Figure on $\{0001\}$	$\{11\bar{2}0\}$	$\{10\bar{1}0\}$
1a~d	100, 50, 20 and 5% HNO_3 (Room temperature)	×	×	×	—	—	—	—
2a	100% HCl (Room temperature)	◎	○	△	5 sec	Figs. 3a, d & e; Photo. 1a	Fig. 3b; Photo. 1b	Fig. 3c; Photo. 1c
2b	50% " (")	◎	○	△	2~3 min.	" ; "	" ; "	" ; "
2c	5% " (")	◎	○	△	15~25 min.	" ; "	" ; "	" ; "
3a~d	100, 50, 20 and 5% *aqua regias* (")	×	×	×	—	—	—	—
4a~c	100, 50 and 2% H_2SO_4 (")	×	×	×	—	—	—	—
4d & e	10 and 5% " (")	◎	○	△	10~15 min.	Fig. 4; Photo. 2	Fig. 3b; Photo. 1b	Fig. 3c; Photo. 1c
5a	100% HF (")	◎	×	×	5~10 min.	Fig. 5	—	Fig. 3c; Photo. 1c
5b	50% " (")	◎	×	×	3~5 min.	Fig. 3d	—	" ; "
5c	5% " (")	×	×	×	—	—	—	—
6a~d	Saturated (100), 50, 10 and 5% aqueous solutions of CrO_3 (Room temperature)	×	×	×	—	—	—	—
7a~c	100, 50 and 5% aqueous solutions of $HNO_3 + CrO_3$ (94:6) (Room temperature)	×	×	×	—	—	—	—
8a~c	Saturated (100), 50 and 5% aqueous solutions of NaOH (Room temperature)	×	×	×	—	—	—	—
8d	Saturated (100%) aqueous solution of NaOH (Boiling temperature)	◎	◎	◎	40 min.	Fig. 6a; Photo. 3a	Fig. 6b; Photo. 3b	Fig. 6c; Photo. 3c

Table 1. Continued.

No.	Etching Reagent* (Temperature)	Sharpness and Suitability of Light Figure on			Optimum Etching Time	Form of Light Figure on		
		$\{0001\}$	$\{11\bar{2}0\}$	$\{10\bar{1}0\}$		$\{0001\}$	$\{11\bar{2}0\}$	$\{10\bar{1}0\}$
8e	50% aqueous solution of NaOH (Boiling temperature)	○	○	○	4 hours	Fig. 6a ; Photo. 3a	Fig. 6b ; Photo. 3b	Fig. 6c ; Photo. 3c
8f	5% ,, (,,)	×	×	×	—	—	—	—
9a~c	Saturated (100), 50 and 5% aqueous solutions of KOH (Room temperature)	×	×	×	—	—	—	—
9d	Saturated (100%) aqueous solution of KOH (Boiling temperature)	◎	◎	◎	20 min.	Fig. 6a ; Photo. 3a	Fig. 6b ; Photo. 3b	Fig. 6c ; Photo. 3c
9e	50% ,, (,,)	○	○	○	2 hours	,, ; ,,	,, ; ,,	,, ; ,,
9f	5% ,, (,,)	×	×	×	—	—	—	—
10a~c	Saturated (100), 50 and 5% aqueous solutions of $ZnCl_2$ (Room temperature)	×	×	×	—	—	—	—
11a	Saturated aqueous solution of $CuCl_2$ (Room temperature)	◎	×	×	5~20 min.	Figs. 5 & 3d		
11b	5% ,, (,,)	×	×	×	—	—	—	—
12a & b	Saturated (100), and 5% aqueous solutions of $NiCl_2$ (Room temperature)	×	×	×	—	—	—	—
13	Saturated aqueous solution of $FeCl_2 \cdot 4H_2O$ (Room temperature)	×	×	×	—	—	—	—
14a & b	Saturated (100), and 5% aqueous solutions of $FeCl_3 \cdot 6H_2O$ (Room temperature)	×	×	×	—	—	—	—
15a & b	Saturated (100) and 5% aqueous solutions of $FeSO_4 \cdot 7H_2O$ (Room temperature)	×	×	×	—	—	—	—
16a & b	Saturated (100) and 5% aqueous solutions of Na_2SO_4 (Room temperature)	×	×	×	—	—	—	—

Table 1. Continued.

No.	Etching Reagent* (Temperature)	Sharpness and Suitability of Light Figure on			Optimum Etching Time	Form of Light Figure on		
		{0001}	{11$\bar{2}$0}	{10$\bar{1}$0}		{0001}	{11$\bar{2}$0}	{10$\bar{1}$0}
17a	Mixture of both saturated aqueous solutions of Na_2SO_4 and of CrO_3 (95:5) (Room temperature)	◎	○	△	>5~10 min.	Fig. 3d	Fig. 3b; Photo. 1b	Fig. 3c; Photo. 1c
17b	” (92:8) (”)	◎	○	○	>1 min.	Figs. 3d & 5	Figs. 3b, 7a & c.	Figs. 3c, 7b & d
17c	” (90:10) (”)	◎	○	○	>3 min.	”	Figs. 7a & c	Figs. 6c & 7d
17d	” (87:13) (”)	◎	○	○	>2 min.	Figs. 3e & d, & 5	Fig. 3b; Photo. 1b	Fig. 3c; Photo. 1c
17e	” (85:15) (”)	◎	○	○	>1 min.	”	Figs. 8a & 3b; Photo. 1b	Figs. 8b & 1c; Photo. 1c
17f	” (80:20) (”)	◎	○	○	>2 min.	”	” ; ”	” ; ”
17g	” (50:50) (”)	○	△	△	1~2 hours	Fig 5	Fig. 3b; Photo. 1b	Fig. 3c; Photo. 1c
18a	Saturated aqueous solution of $(NH_4)_2S_2O_8$ (Room temperature)	×	×	×	—	—	—	—
18b & c	50 and 5% ” (”)	◎	×	×	10~20 min.	Fig. 3d	—	—

* Concentration of an etching solution is expressed in relative to that of a concentrated acid or of a saturated aqueous solution of an alkali or salt as 100 percent.

hydroxide], and of salts [(10) zinc chloride, (11) cupric chloride, (12) nickel chloride, (13) ferric chloride, (14) ferrous chloride, (15) ferric sulphate, (16) sodium sulphate, (17) mixture of sodium sulphate and chromic acid anhydride, and (18) ammonium persulphate], concentrations[5] and temperatures of which are shown in Table 1.

Specimen crystals were etched beforehand with concentrated nitric acid for several seconds (or with 50 percent[5] nitric acid for about 10 seconds) in order to keep their initial states all the same. This preliminary etching produces a blank etching so that grain boundaries are not developed in polycrystalline zinc and no light figures can be observed with monocrystalline zinc. Crystals once etched with a certain reagent were subjected to the preliminary etching before they were tested again with any other reagent. Several specimen crystals thus treated preliminarily were dipped into an etching solution at the same time and, after an elapse of proper time they were picked up, washed with running water and then dried. Then, they were mounted on the apparatus for producing and observing light figures, as described previously[6], which was set in a dark room. Light figures on the three principal crystallographic planes (0001) $(11\bar{2}0)$ and $(10\bar{1}0)$ were at first observed by naked eyes and then sketched or printed directly on photographic papers of ordinary sensitiveness when necessary. It is to be noted that light figures are really seen as bright on a black ground, but their sketches and photographs as shown later are conveniently made as black on a white ground. This procedure was repeated at appropriate etching time-intervals.

Colours of light figures of zinc crystals are generally yellow and the time of exposure for printing is at most 20 minutes, for a white-light source of 500 watts.

III. Experimental Results

(1a—d) 100, 50, 20 and 5 percent nitric acids (room temperature).

No light figure is observed with zinc crystals etched with concentrated nitric acids (100—20%), since the etching power of these reagents is considerably strong and the surface of crystals is made blank. The effect of dilute nitric acid (5%) is different from that of concentrated ones. A black film is produced on the surface of crystals, and consequently only indistinct light figures are obtained even after etching for several hours.

(2a) 100 percent hydrochloric acid (room temperature).

We obtain distinct light figures on the three principal crystallographic planes of zinc crystals etched for a very short time (2—3 seconds) with concentrated hydrochloric acid. In the figure of {0001} plane six lines radiate from apexes of a hexagon with a tiny spot

(5) In this report, concentrations of etching solutions are conveniently expressed in relative to those of commercial "concentrated" acids or saturated aqueous solutions of alkalis or salts as 100%. True concentrations of "concentrated" nitric acid, hydrochloric acid, sulphuric acid and hydrofluoric acid employed are 61.4, 29.6, 95.6 and 40 percent, respectively.

(6) M. Yamamoto, Sci. Rep. Tohoku Imp. Univ., 29 (1941), 113; 31 (1943), 121.

at its center (Fig. 3a[7] and Photo.1a[8]), in that of $\{11\bar{2}0\}$ plane two arcs lie on both sides of a halo circle (Fig. 3b and Photo. 1b), and that of $\{10\bar{1}0\}$ plane is a straight line (Fig. 3c and Photo. 1c). It hardly needs to say that the line-like $\{10\bar{1}0\}$ figure appears as the six-line radiation in the $\{0001\}$ figure and as the two arcs in the $\{11\bar{2}0\}$ figure.

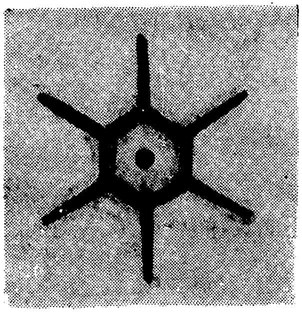

Fig. 3a. {0001}, 100% HCl, 5 sec.

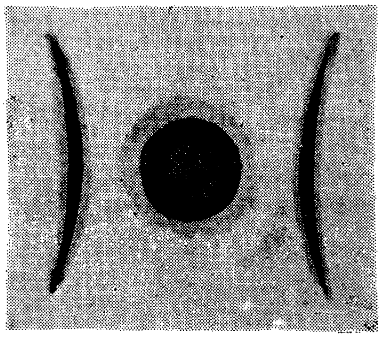

Fig. 3b. $\{11\bar{2}0\}$, 100% HCl, 5 sec.

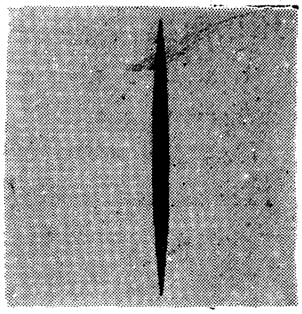

Fig. 3c. $\{10\bar{1}0\}$, 100% HCl, 5 sec.

With the continuation of etching over about 5 seconds, the surface of crystals become rough and, moreover, are covered with a black film, and consequently the distinctness of the light figures diminishes gradually. At the etching time of about 10 seconds

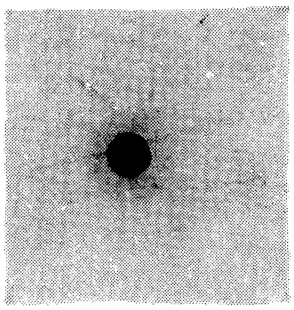

Fig. 3d. {0001}, 100% HCl, 10 sec.

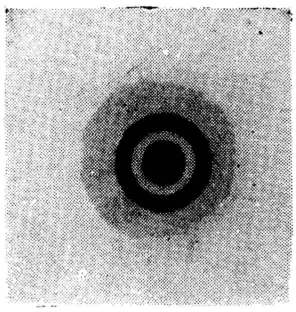

Fig. 3e. {0001}, 100% HCl, 10 sec.

the $\{0001\}$ light-figure changes to a simple tiny spot or a ring with a tiny spot at its center (Figs. 3d and e). Finally, we can hardly observe any light figure at 20 minutes.

It should be noted that the $\{0001\}$ figure obtained by etching for about 5 seconds with this reagent is suitable for determining an angle θ which the geometrical axis of a zinc crystal makes with its hexagonal axis $\langle 0001 \rangle$[9]

(7) Specifications of figures and photographs of light figures are, for brevity, made in the order of the crystal plane by which the light figure was produced, the reagent with which zinc crystals were etched, and the time of etching.

(8) Photographs of light figures are shown *en bloc* at the end of this paper.

(9) The light figures on $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ planes are distinct, but insufficient or unsuitable for the determination of angles α, β and γ which the geometrical axis of a specimen crystal makes with the digonal axes of the first kind $\langle 11\bar{2}0 \rangle$, since those figures have no definite center of symmetry.

(2b and c) 50 and 5 percent hydrochloric acids (room temperature).

Zinc crystals etched with 50 percent hydrochloric acid for several minutes or with dilute (5%) hydrochloric acid for 15~30 minutes produce celar light figures on all principal crystal planes, quite analogous to those obtained in the case of concentrated one, (Figs. 3a~c; Photos. 1a~c). Notably, the {0001} figure in these cases is more distinct and suitable for determining an angle θ between the geometrical and hexagonal axes of zinc crystals. Further continuation of etching make the light figures indistinct rapidly as a black surface-film is produced.

(3a~d) 100, 50, 20 and 5 percent aqua regias (room temperature).

The aspect of etching zinc crystals by more concentrated aqua regias (100~20%) are nearly the same as in the case of concentrated nitric acids,(10) while the etching by dilute (5%) aqua regia is almost similar to that by dilute nitric acid.

(4a~c) 100, 50, and 20 percent sulphuric acids (room temperature).

The etching of zinc crystals by more concentrated (100~20%) sulphuric acids is very slow and we can observe only very indistinct light figures even after etching for a prolonged period.

(4d and e) 10 and 5 percent sulphuric acids (room temperature).

The etching with dilute sulphuric acids (10 and 5%) is entirely different from that with concentrated ones, and distinct light figures are obtained after 10~15 minutes. The (0001) figure has such a characteristic form as shown in Fig. 4 and Photo. 2 and is suitable for determining θ, while the {11$\bar{2}$0} and {10$\bar{1}$0} figures are quite similar to those obtained by etching with hydrochloric acids (Figs. 3b and c; Photos. 1b and c). The further increase of the etching-time makes the surface of crystals rough and consequently the distinctness of the light figures decreases gradually.

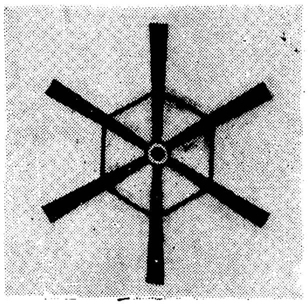

Fig. 4. {0001}, 10% H_2SO_4, 10 min

(5a) 100 percent hydrofluoric acid (room temperature).

Etching for several minutes with this reagent produces distinct light figures on {0001} and {10$\bar{1}$0} planes of zinc crystals ,the surface of which has coloured grey-white. In the {0001} figure six weak lines radiate from a distinct spot (Fig. 5) and the {10$\bar{1}$0} figure is of a linear-like one similar to that obtained by etching with hydrochloloric acids (Fig. 3c and Photo. 1c). The continuation of etching makes the light figures indistinct gradually. It is to be noted that the {0001} figure is suitable for the determination of an angle θ, and that the {11$\bar{2}$0} figure is not observed.

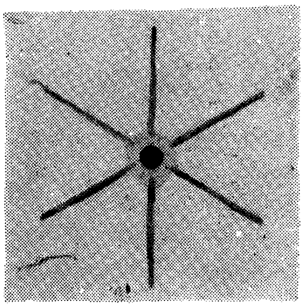

Fig. 5. {0001}, 100% HF, 5~10 min.

(5b and c) 50 and 5 percent hydrofluoric acids (room temperature).

(10) There is only one difference that a film sticks to the surface of crystals in the case of aqua regias.

With zinc crystals etched with 50 percent hydrofluoric acid for about 3 minutes, we observe a distinct light spot on $\{0001\}$ plane (Fig. 3d), a slightly dim linear figure on $\{10\bar{1}0\}$ plane (Fig. 3c), and no figure on $\{11\bar{2}0\}$ plane. The $\{0001\}$ figure is suitable for determining an angle θ. While, dilute (5%) hydrofluoric acid produces indistinct light figures only on $\{0001\}$ and $\{10\bar{1}0\}$ planes even after a prolonged period.

(6a～d) Saturated (100 percent), 50, 10 and 5 percent aqueous solutions of chromic acid anhydride (from temperature).

In the case of etching with any concentrated aqueous solution of chromic acid anhydride, no light figure is observed on account of a white film produced on the surface of crystals.

(7a～c) 100, 50 and 5 percent aqueous solutions of the mixture of nitric acid and chromic acid anhydride (94 : 6) (room temperature).

The etching effects of these mixed solutions for zinc crystals are quite analogeous to those of nitric acids (1a～d), and no or indistinct light figures are observed.

(8a～c) Saturated (100 percent), 50 and 5 percent aqueous solutions of sodium hydroxide (room temperature), or (9a～c) of potassium hydroxide (room temperature).

Even after etching for 7 days, only indistinct light figures are observed, since a black film is produced on the surface of crystals.

(8d) Saturated aqueous solutions of sodium hydroxide, and (9d) of potassium hydroxide (both boiling temperature).

By etching zinc crystals for 20 minutes with boiling saturated solution of potassium hydroxide or for 40 minutes with similar solution of sodium hydroxide, we obtain on their $\{0001\}$, $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ planes distinct light figures of such characteristic forms as shown in Figs. 6a～c and Photos. 3a～c. With the further increase of the etching-

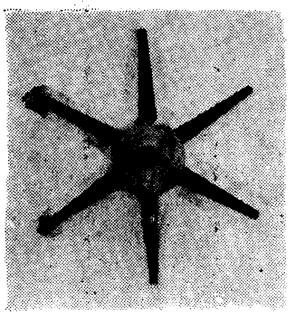

Fig. 6a. $\{0001\}$, sat. aq. sol. of KOH (boiling), 20 min.

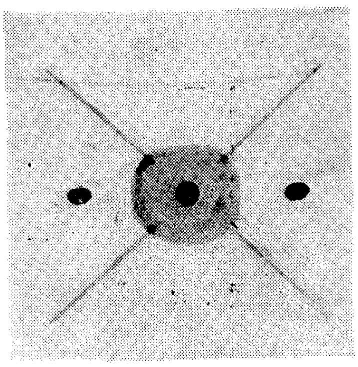

Fig. 6b. $\{11\bar{2}0\}$, sat. aq. sol. of KOH (boiling), 20 min.

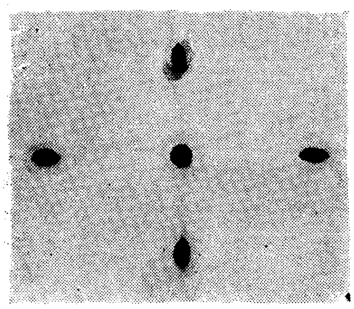

Fig. 6c. $\{10\bar{1}0\}$, sat. aq. sol. of KOH (boiling), 20 min.

time, the $\{0001\}$ figure changes to a tiny spot (Fig. 3d) and the $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ figures diminish their clearness gradually. At one hour with potassium-hydroxide solution or at one hour and a half with sodium-hydroxide solution, all light figures vanish because of the blank etching resulted. It must be noted that light figures on the three principal planes obtained by etching with potassium-hydroxide soultion or with sodium-hydroxide one are the most suitable for the perfect determination of crystal orientations of zinc crystals.

(8e) 50 percent aqueous solutions of sodium hydroxide, and (9c) of potassium hydroxide (both boiling temperature).

Light figures similar to those obtained in the case of boiling saturated solutions are observed by etching for 2 hours with potassium-hydroxide solution or for 4 hours with sodium-hydroxide solution, though they are slightly indistinct. Changes of light figures with the continuation of etching are also quite similar.

(8f) 5 percent aqueous solutions of sodium hydroxide, and (9f) of potassium hydroxide (both boiling temperature).

Since a black film produced on the surface of zinc crystals by etching with a dilute aqueous solution of sodium hydroxide or of potassium hydroxide can not be easily removed, light figures observed are very indistinct.

(10a—c) Saturated (100), 50 and 5 percent aqueous solutions of zinc chloride (room temperature).

The etching with saturated aqueous solution of zinc chloride produces only on base plane an indistinct light figure of a halo-circle form at 10 minutes and an indistinct figure similar to that obtained by etching with concentrated hydrofluoric acid (Fig. 5) at 7 hours. While, a long-time etching with more dilute solutions produce a very indistinct light figure only on base plane.

(11a and b) Saturated (100) and 5 percent aqueous solutions of cupric chloride (room temperature).

By etching zinc crystals with saturated solution of cupric chloride for 5 minutes a distinct tiny spot (Fig. 3d), suitable for determining an angle θ, is observed on base plane, this figure soon changing to a form similar to that obtained in the case of concentrated hydrofluoric acid (Fig. 5). A light figure of a linear-like form on $\{10\bar{1}0\}$ plane is always indistinct and that on $\{11\bar{2}0\}$ plane is hardly observed. In the case of dilute solution, no light figure is observed even after a long-time etching.

(12a and b) Saturated (100) and 5 percent aqueous solutions of nickel chloride, (13) Saturated aqueous solution of ferrous chloride, (14a and b) saturated (100) and 5 percent aqueous solutions of ferric chloride, and (15a and b) of ferrous sulphate (all room temperature).

In cases of etching with these solutions, we obtain very indistinct or no light figures.

(16a and b) Saturated (100) and 5 percent aqueous solutions of sodium sulphate (room temperature).

We obtain an indistinct light figure of a halo-circle form on base plane alone by etching with saturated aqueous solution of sodium sulphate over 5 minutes. While, dilute solution is inactive to zinc and no light figure is observed.

(17a) Mixture of both saturated aqueous solutions of sodium sulphate and of chromic acid anhydride (95 : 5) (room temperature).

Distinct light figures are observed on all principal crystallographic planes by etching with this reagent for 5—10 minutes. The {0001} figure is a tiny spot (Fig. 3d), suitable for determining an angle θ, and {11$\bar{2}$0} and {10$\bar{1}$0} figures are similar to those obtained in the case of hydrochloric acids (Figs. 3b and c; Photos. 1b and c). A further etching makes the surface of crystals grey and the light figures become indistinct.

(17b) Mixture of both saturated aqueous solutions of sodium sulphate and of chromic acid anhydride (92 : 8) (room temperature).

Light figures produced by etching with this mixed solution for several minutes are quite analogeous to those obtained in the case of above-mentioned 95 : 5 solution (Figs. 3d, b and c; Photos. 1b and c). On the continuation of the etching over one hour, the {0001} figure, a tiny spot, becomes obscure and then six lines appear from its circumference (Fig. 5), while {11$\bar{2}$0} and {10$\bar{1}$0} figures change to such forms as shown in Figs. 7a and b and afterwards to shapes as shown in Figs. 7c and d. But, at the time

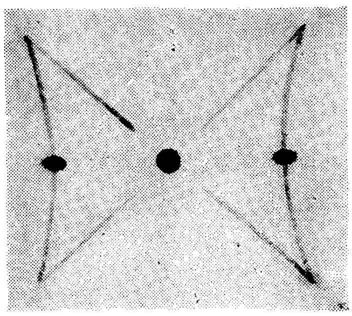

Fig. 7a. {11$\bar{2}$0}, sat. aq. sol. of Na_2SO_4+sat. aq. sol. of CrO_3 (92:8), 20 hr.

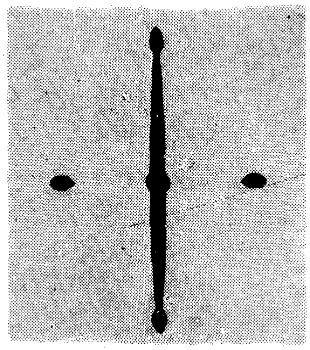

Fig. 7b. {10$\bar{1}$0}, sat. aq. sol. of Na_2SO_4+sat. aq. sol. of CrO_3 (92:8), 20 hr.

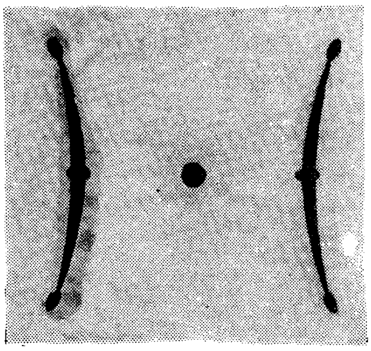

Fig. 7c. {11$\bar{2}$0}, sat. aq. sol. of Na_2SO_4+sat. aq. sol. of CrO_3 (92:8), 24 hr.

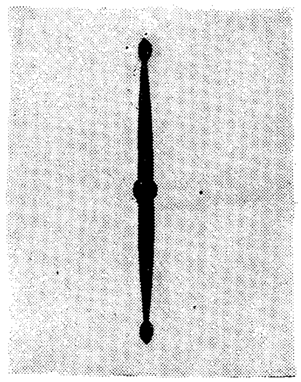

Fig. 7d. {10$\bar{1}$0}, sat. aq. soi. of Na_2SO_4+sat. aq. sol. of CrO_3 (92:8), 24 hr.

of etching over 24 hours these figures return to forms similar to those observed by a short-time etching, though their distinctness is shortened.

(17c) Miture of both saturated aqueous solutions of sodium sulphate and of chromic acid anhydride (90 : 10) (room temperature).

A distinct but tiny spot is observed on base plane by etching with this reagent for 3 minutes. Indistinct light figures, whose forms are as shown above in Figs. 7a and 6c, appear on prism planes of the first and second kinds by 10-minutes etching. Variations of these figures with the further increase of the etching time are similar to the above-described case of 92 : 8 solution.

(17d) Mixture of both saturated aqueous solutions of sodium sulphate and of chromic acid anhydride (87 : 13) (room temperature).

By etching for 2 minutes a distinct light figure of a ring form (Fig. 3e) is observed on base plane, and by further etching this figure changes through a distinct spot form (Fig. 3d) to a form as shown in Fig. 5. The {0001} figure is suitable for determining an angle θ. On the other hand, indistinct light figures on prism planes of both kinds, produced by etching for 5 minutes, have the same forms as those obtained by a long-time etching with 92 : 8 solution (Figs. 7c and d), and change to distinct figures similar to those obtained in the case of hydrochloric acids (Figs. 3b and c) at the etching time over 15 minutes. The further etching has no influence on the clearness of these light figures.

(17e and f) Mixtures of both saturated aqueous solutions of sodium sulphate and of chromic acid anhydride (85 : 15 and 80 : 20) (room temperature).

The form of light figure on base plane and its change with an increase of the time of etching are quite similar to the case of 87 : 13 solution. Both {11$\bar{2}$0} and {10$\bar{1}$0} figures

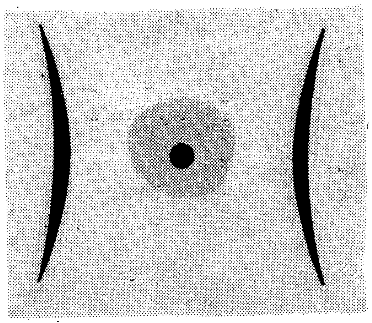

Fig. 8a. {11$\bar{2}$0}, sat. aq. sol. of Na_2SO_4 + sat. aq. sol. of CrO_3 (85:15), 1.5 hr.

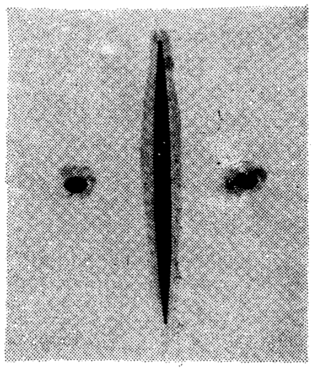

Fig. 8b. {10$\bar{1}$0}, sat. aq. sol. of Na_2SO_4 + sat. aq. sol. of CrO_3 (85:15), 1.5 hr.

observed at the etching time of 1.5 hours are as shown in Figs. 8a and b, and those at 8 hours' etching are similar to figures obtained in the case of hydrochloric acid (Figs. 3b and c; Photos. 1b and c). The {0001} figure is suitable for the determination of an angle θ.

(17g) Mixture of both saturated aqueous solutions of sodium sulphate and chromic acid anhydride (50 : 50) (room temperature).

Distinct light figures approximately similar to those obtained by etching with hydrochloric acids (Figs. 5, 3b and c; Photos. 1b and c) are observed on the three principal crystallographic planes by etching for 1～2 hours. The {0001} figure is insufficient for determining an angle angle θ because of a long-time etching required.

(18a—c) Saturated (100), 50 and 5 percent aqueous solutions of ammonium persulphate (room temperature).

In an etching with saturated solution of ammonium persulphate, the surface of zinc crystals is covered with a thin film, and so any light figures observed are very indistinct. By etching with more dilute (50 and 5 percent) solutions for about 10—20 minutes we obtain a tiny spot (Fig. 3d) on base plane and figures similar to those obtained in the case of hydrochloric acid (Figs. 3b and c) on prism planes of both kinds.

The experimental results described above are summarized in Table 1, in which the mark ◎ denotes a distinct light figure, suitable to the determination of crystal orientations, ○ also a distinct figure, but not so suitable, △ a distinct, but unsuitable figure and × an indistinct or no figure.

First, we can not observe any light figure on the three principal crystallographic planes of zinc crystals etched with one of the following reagents:

(1a—c) concentrated nitric acids, (7a) mixture of nitric acid and chromic acid anhydride (94 : 6), (3a—c) more concentrated *aqua regias,*	I
(6a—d) variously concentrated aqueous solutions of chromic acid anhydride, (12a and b) variously concentrated aqueous solutions of nickel chloride, (14a and b) variously concentrated aqueous solutions of ferrous sulphate,	II
(11b) dilute aqueous solution of cupric chloride, and (16b) dilute aqueous solution of sodium sulphate.	III

These reagents may be classified into three groups, as indicated above, as regard to their effect on zinc crystals. The group I make the surface of crystals blank, the group II produce a thick film on the surface of crystals, and the group III are almost inactive to crystals.

Next, we obtain indistinct light figure only on $\{0001\}$ plane and no figure on $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ planes in cases of etching with one of the following reagents: (10a—c) variously concentrated aqueous solutions of zinc chloride, and (13) saturated aqueous solutions of ferorus chloride, (16a) of sodium sulphate and (18a) of ammonium persulphate.

On the other hand, we can not obtain any light figure on $\{11\bar{2}0\}$ plane of zinc crystals etched with (5a—c) hydrofluoric acids of any concentration.

Further, light figures produced on the three principal crystal planes of zinc crystals etched with one of the following reagents are very indistinct: (1d) dilute nitric acid, (3d) dilute *aqua regia,* (4a) concentrated sulphuric acid, (7b and c) dilute aqueous solutions of mixtures of nitric acid and chromic acid anhydride (94 : 6), and (8a—c) variously concentrated aqueous solutions of sodium hydroxide, (9a—c) of potassium hydroxide, and (14a and b) of ferric chloride. These reagents are common in that the etching power for zinc crystals is very weak and a thick film sticks to the surface of crystals.

While, we can observe distinct light figures on the three principal crystallographic planes of zinc crystals etched with one of the following reagents: (2a—e) variously concentrated hydrochloric acids, (4d and e) dilute sulphuric acids, (8d and e) concentrated aqueous solutions of sodium hydroxide (boiling) and (9d and e) of potassium hydroxide (boiling), and (17b—f) mixtures of both saturated aqueous solutions of sodium sulphate and chromic acid anhydride (92 : 8—80 : 20).

Distinct light figures on {0001} plane, produced by a short-time etching with one of just-mentioned reagents and (5a and b) concentrated hydrofluoric acids, (11a) saturated aqueous solutions of sodium sulphate and chromic acid anhydride (95 : 5), and (18b and c) dilute aqueous solutions of ammonium persulphate, is suitable for determining and angle θ which the geometrical axis of a crystal specimen makes with the hexagonal axis ⟨0001⟩. Light figures the most suitable for determining angles α, β and γ between the axis of a specimen and digonal axis of the first kind ⟨11$\bar{2}$0⟩ are those on {11$\bar{2}$0} and {10$\bar{1}$0} planes obtained by etching with reagents (8d and e) or (9d and e). {11$\bar{2}$0} and {10$\bar{1}$0} figures obtained in other cases are insufficient or unsuitable for determining α, β and γ owing to their indistinctness or inadequate form or the long etching-time required. Accordingly, for the perfect determination of crystal orientations of zinc crystals, light figures obtained by etching for 40 or 20 minutes with boiling saturated aqueous solution of sodium hydroxide or of potassium hydroxide are the most suitable.

It is to be noted that every light figure on base plane has the hexagonal symmetry and that on prism planes of both kinds the digonal symmetry, and that their symmetry characteristics are naturally invariable, though their geometrical forms change with etching conditions, that is, the etching reagent, its temperature and the time of etching.

As mentioned above, in some cases the distinctness of light figures on the three principal crystal planes is remarkably different from each other or figures on certain crystal planes are harly observed, even by the same etching. These facts naturally arise from the anisotropy of chemical property of zinc crystals and it may be seen that the {0001} plane is the least resistant and the {11$\bar{2}$0} plane is the most resistant, to reagents.

Aqueous solutions of sodium hydroxide or potassium hydroxide produce only indistinct light figures at room temperature, but very distinct figures at boiling temperature. This shows that the effect of alkalis on zinc is the oxidation by OH^- and K^+ or Na^+ is not concerned with.

Among aqueous solutions of metal salts tested, only a saturated aqueous solution of cupric chloride produces relatively clear light figures. This may be due to the fact that the ionizing power of copper is larger than that of zinc.

Summary

Light figures were observed on the three principal crystallographic planes {0001}, {11$\bar{2}$0} and {10$\bar{1}$0} of zinc crystals, which were etched for various time-intervals with variously concentrated aqueous solutions of various acids, alkalis and salts, and the suit-

ability of those figures for the determination of crystal orientations by the method of light figures was examined. The experimental results are summarized in Table 1.

Clear light figures, suitable for determining an angle θ between the geometrical axis of a crystal and the hexagonal axis $\langle 0001 \rangle$, are obtained on $\{0001\}$ plane of zinc crystals by a short-time etching with one of following reagents: (1) variously concentrated hydrochloric acids, (2) dilute sulphuric acids, (3) concentrated hydrofluoric acids, (4) boiling saturated aqueous solutions of sodium hydroxide or of potassium hydroxide, (5) saturated aqueous solution of cupric chloride, (6) mixtures of both saturated aqueous solutions of sodium sulphate and chromic acid anhydride (95 : 5～80 : 20), (7) dilute aqueous solutions of ammonium persulphate. Reagents (1), (2), (4), and (6) also produce distinct light figures on $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ planes, but only light figures produced by reagents (4) are suitable for determining angles α, β and γ between the geometrical axis of a crystal and the diagonal axes of the first kind $\langle 11\bar{2}0 \rangle$.

Every light figure observed on base plane of zinc crystals has the hexagonal symmetry and that on prism planes of the first and second kinds the digonal symmetry. Their symmetry characteristics are naturally invariable, though their forms vary with etching conditions.

In conclusion, it is to be added that the present investigation was helped partially by the fund granted by the Ministry of Education.

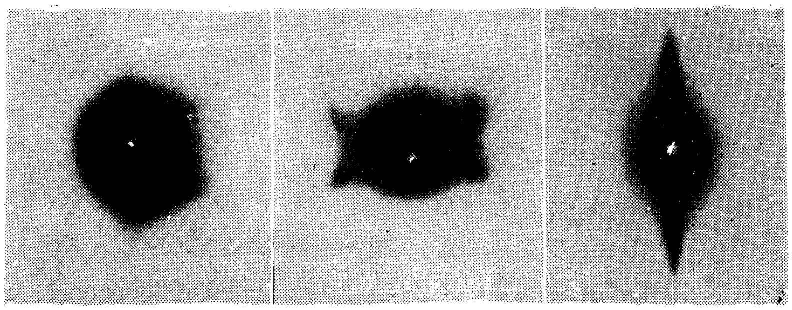

Photo. 1a. $\{0001\}$, 50% HCl, 2 min.
Photo. 1b. $\{11\bar{2}0\}$, 50% HCl, 2 min.
Photo. 1c. $\{10\bar{1}0\}$, 50% HCl, 2 min.

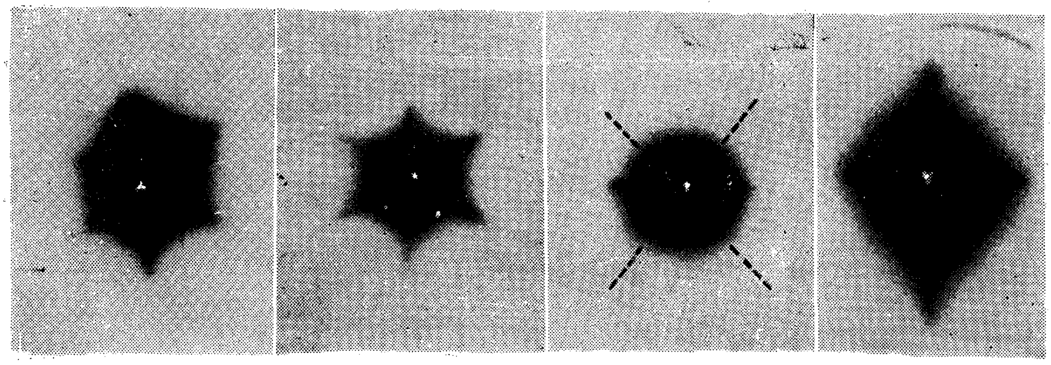

Photo. 2. $\{0001\}$, 5% H_2SO_4, 10 min.
Photo. 3a. $\{0001\}$, sat. aq. sol. of KOH (boiling), 20 min.
Photo. 3b. $\{11\bar{2}0\}$, sat. aq. sol. of KOH (boiling), 20 min.
Photo. 3c. $\{10\bar{1}0\}$, sat. aq. sol. of KOH (boiling), 20 min.