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On the Biaxialization of Zircon

By

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Abstract

In the course of the metamictization lattice expansion takes place. The expansion is anisotropic in zircon. Biaxial zircon results from the anisotropic expansion of the lattice.

Introduction

DAMOUR[1] (1864) found that zircon was variable in density and low density zircon increased in density by heating. He conceived that there would be various molecular stages in zircon. CHURCH[2] (1875) observed, however, that especially low density zircon remained constant in density by heating. STEVANOVIĆ[3] (1903) divided zircon into three groups as follows:

a-zircon : specific gravity about 4.0, by heating it remains constant, uniaxial before and after heating, incandescent.

b-zircon : specific gravity about 4.7, by heating it remains constant, uniaxial before and after heating, not incandescent.

c-zircon : specific gravity between these two limits, by heating it approaches to upper limit, biaxial partially uniaxial, biaxial portions turn to uniaxial after heating, some specimen incandescent.

STEVANOVIĆ supposed *a*-zircon consisted of an element closely allied to zirconium instead of the zirconium. In this connection KOECHLIN[4] (1903) considered *c*-zircon might be a mixture of *a*-zircon and *b*-zircon. SPENCER[5] (1904) made observations on zircon and approved of the division proposed by STEVANOVIĆ. MÜGGE[6] (1922) was doubtful of the three groups in zircon. According to him, *b*-zircon may be non-affected zircon by the alpha particles, hence, may be normal, *c*-zircon may be more or less affected one, however, not decomposed chemically preserving lattice remnants and *a*-zircon may be fully metamictized one.

CHUDOBA and VON STACKELBERG[7] (1936) and VON STACKELBERG and CHUDOBA[8] (1937) made careful observations on zircon. *b*-zircon was uniaxial and partially biaxial, *c*-zircon was biaxial and partially uniaxial and *a*-zircon was isotropic. Upon the X-ray photographs *b*-zircon and *c*-zircon gave essentially the same patterns, however, one a-zircon gave no pattern, another a-zircon gave cubic ZrO_2 pattern together with very weak zircon pattern. Being heated to 1450°C, both a- and c-zircon increased in density and gave the same patterns that b-zircon gave. They concluded that a- and c-zircon arose from b-zircon through the metamictization, however, in c-zircon it was in progress and in a-zircon it was finished. LIETZ[9] (1938) and BAUER[10] (1939) studied on zircon and confirmed the results obtained by CHUDOBA and VON STACKELBERG. BAUER kept zircon on the photographic film for about a month and found after development of the film that the low density specimens blackened the film more intensively. On the basis of this observation BAUER was of the opinion that the low density zircon arose from the normal zircon through the metamictization.

WEIGEL[11] (1938) inquired into the relationship between the density and the radioactivity in zircon. Specimens low in density were always stronger in radioactivity than those high in density. MORGAN and AUER[12] (1941) examined the relationship between optical properties and radioactivity in zircon and found that specimen the highest in refringence and the strongest in birefringence showed the lowest radioactivity, lower in refringence and weaker in birefringence higher radioactivity and the lowest in refringence and the weakest in birefringence the highest radioactivity.

Summarizing the results obtained by these previous authors, it is hardly to doubt that biaxial zircon arose from the normal zircon in the course of the metamictization. However, no one has ever examined whether the ratio of the lateral axes actually varies with progress of the metamictization. Recently the author has found that in the course of the metamictization lattice of zircon expanded anisotropically and the crystal became biaxial.

Experimental

Specimens submitted to the present examination are as follows. They are in the range from 4.66 to 4.18 in the specific gravity.

Locality	Specific gravity
Burma	4.66
Omiya-chô (Morimoto), Kyoto Pref.	4.40
Hagata-mura, Ehime Pref.	4.38
Mineyama-chô (Oro), Kyoto Pref.	4.24
Omiya-chô (Kôbe), Kyoto Pref.	4.21
Yamaguchi-mura, Nagano Pref.	4.20
Ishikawa-chô, Fukushima Pref.	4.18
Otsu-shi (Shimotanakami), Shiga Pref.	4.18
Nakatsugawa-shi (Naegi), Gifu Pref.	4.24

With each of the specimens a portion was cut off and provided for the measurement of $2V$. Unit cell dmeinsions were measured by means of the

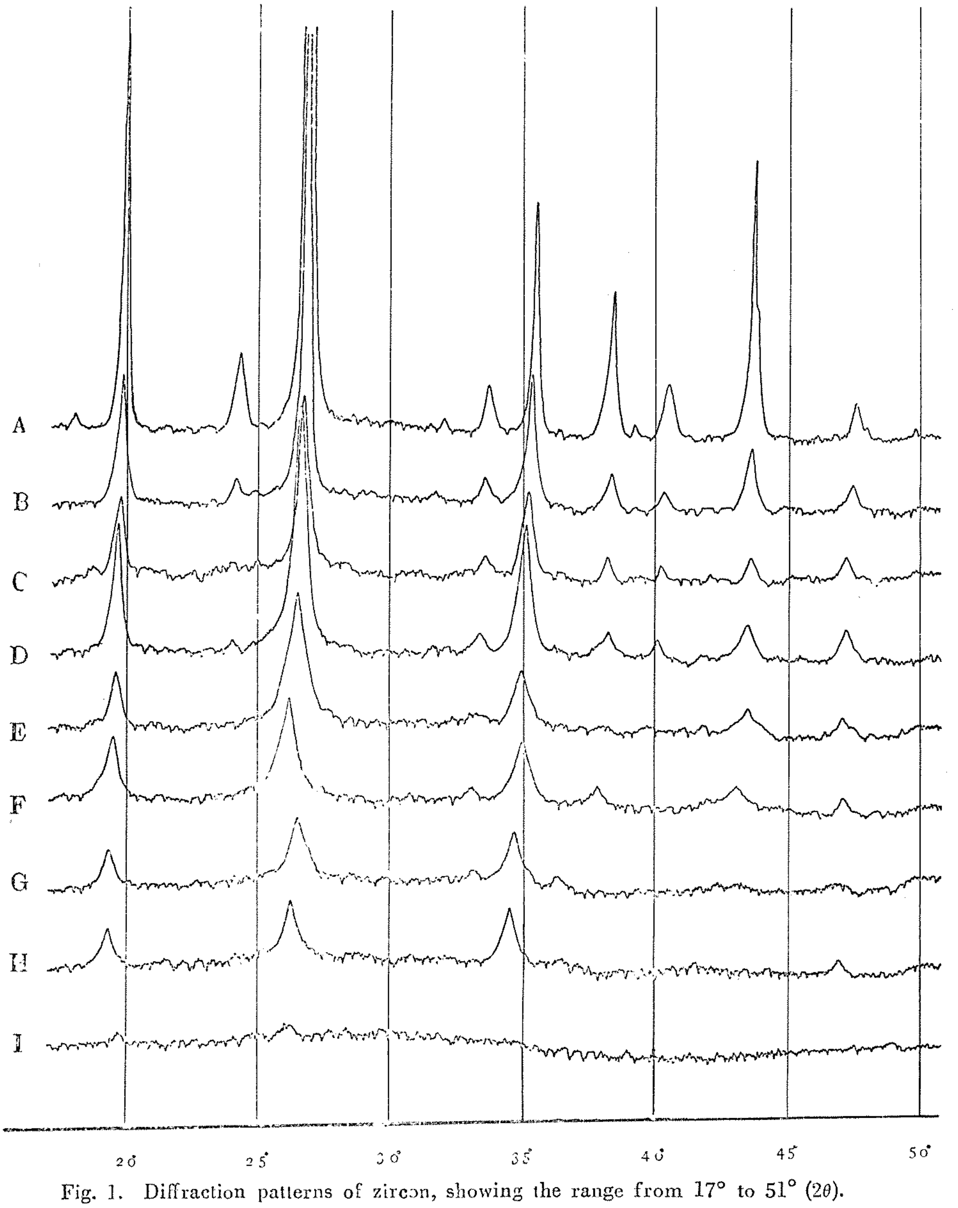

Fig. 1. Diffraction patterns of zircon, showing the range from 17° to 51° (2θ).

A: Burma
B: Omiya-chô (Morimoto)
C: Hagata-mura
D: Mineyama-chô (Oro)
E: Omiya-chô (Kôbe)
F: Yamaguchi-mura
G: Ishikawa-chô
H: Otsu-shi (Shimotanakami)
I: Nakatsugawa-shi (Naegi)

X-ray powder photographing using Norelco Geiger counter X-ray spectrometer of North American Philips Co. In the use of the spectrometer, following conditions were adopted.

voltage : 30 kV
current : 15 mA
radiation : Cu–$K\alpha$
scanning speed : 1° per minute
chart speed : 1/2 inch per minute
scale factor : 8
multiplier : 1
time constant : 8 second
slit : 1°—0.006″—1°

Pulverization of the specimens was carefully carried out so that the powders might not differ in size with different specimens. Packing of the powders into hollow of the glass plate was also carefully so that the powders might not differ in compactness with different specimens. The diffraction patterns of these specimens are arranged in Fig 1, however, only in the range from 17° to 51° (2θ).

As will be seen in Fig. 1, peaks in the diffraction patterns are widely different in sharpness and in height. Since the metamictization is a gradual change of the crystal state into amorphous one, sharpness and height of the peaks in the diffraction pattern represent the degree of the metamictization of the specimen. Comparing the diffraction patterns shown in Fig. 1 with one another, it is noticeable that the peaks shift more and more towards low angle side as they decrease in sharpness and in height. This shows that lattice of zircon expands as the metamictization goes on. 2θ angles were measured at the maxima of the peaks and calibrated by the silicon diffraction pattern using the method of least squares. In some specimens peaks in the diffraction patterns were asymmetrical in shape and frequently splitted into branchlets, suggesting that the distribution of the radioactive elements in the specimen is intensely heterogeneous. In Fig. 2 is shown such diffraction pattern as an example. In the present examination measurements with such patterns were abandoned.

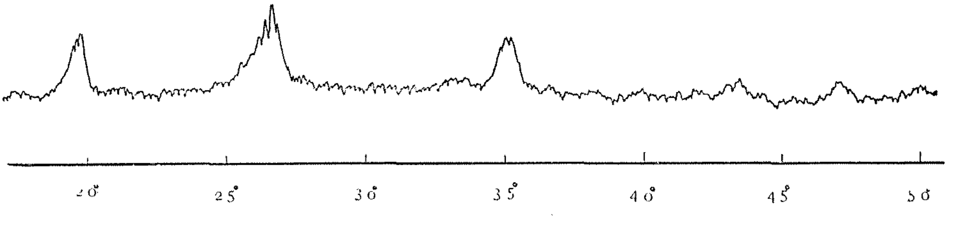

Fig. 2. Diffraction pattern of zircon in which peaks are asymmetrical splitting into branchlets.

Indices of the reflexions which brought forth these peaks were calculated making use of the result of the structure analysis carried out by VEGARD[13] (1926). In Table 1 are shown the indices of the reflexions and their $\sin^2\theta$ -values.

Table 1. $\sin^2\theta$-values of the reflexions in the diffraction patterns of zircon.

hkl	sin 2θ							
	A	B	C	D	E	F	G	H
101	.03024	.03006	.03005	.02976	.02966	.02945	.02887	.02887
200	.05438	.05436	.05397	.05357	.05357	.05266	.05344	.05344
211	.08468	.08419	.08134	.08321	—	.08209	—	—
112	.09364	.09278	.09243	.09210	.09110	.09160	.08976	.08976
220	.10903	.10833	.10707	.10725	—	.10528	—	—
202	.12076	.11961	.11942	.11829	—	—	—	—
301	.13935	.13832	.13852	.13672	.13691	.13452	—	—
103	.16305	.16135	.16050	.16006	.15922	.15986	.15834	.15836
321	.19378	.19262	.19171	.18938	.18875	.18760	.18920	.18920
312	.20259	.20119	.20049	.19933	.19909	.19654	.19770	.19909
213, 400	.21800	.21679	.21583	.21368	—	.21060	—	—

A: Burma　　B: Omiya-chô (Morimoto)
C: Hagata-mura　　D: Mineyama-chô (Oro)
E: Omiya-chô (Kôbe)　　F: Yamaguchi-mura
G: Ishikawa-chô　　H: Otsu-shi (Shimotanakami)

Cell-dimensions of the specimens were calculated from the $\sin^2\theta$-values by the following equation using the method of least squares.

$$4\sin^2\theta = h^2 a_1^{*2} + k^2 a_2^{*2} + l^2 c^{*2}$$

Results are shown in Table 2 in which cell-dimensions determined by VEGARD are inserted for comparison. Now, it is clear that cell-dimensions of zircon increase progressively as the metamictization goes on, however, the lattice expansion takes place anisotropically. In Table 3 are shown the rates of increase of a_1, a_2 and c taking the cell-dimensions determined by VEGARD as standard, and the ratios of $a_1 : a_2$.

Optical observations were carried out with thin sections cut off perpendicular to c-axis, using universal stage. Under the cross nicols specimens from Burm and Mineyama-chô (Oro) proved in every portion of the thin sections to be always dark. In other specimens interference colour was observed. With such

Table 2. Cell-dimensions and cell-volumes of zircon.

	VEGARD	A	B	C	D	E	F	G	H
a_1	6.59 Å	6.600	6.620	6.616	6.660	6.645	6.717	6.657	6.623
a_2	6.59 Å	6.595	6.612	6.678	6.658	6.776	6.704	6.730	6.803
c	5.94 Å	5.974	6.001	6.016	6.032	6.043	6.049	6.080	6.078
V	257.96 $Å^3$	260.03	262.67	265.80	267.47	272.32	272.39	272.39	273.85

A: Burma B: Omiya-chô (Morimoto)
C: Hagata-mura D: Mineyama-chô (Oro)
E: Omiya-chô (Kôbe) F: Yamaguchi-mura
G: Ishikawa-chô H: Otsu-shi (Shimotanakami)

Table 3. Rates of increase of cell-dimensions, ratios of $a_1 : a_2$ and $2V$-values in zircon.

	A	B	C	D	E	F	G	H
a_1	0.15%	0.46	0.39	1.06	0.83	1.93	1.02	0.50
a_2	0.08%	0.33	1.34	1.03	2.82	1.73	2.12	3.23
c	0.57%	1.03	1.28	1.55	1.82	1.84	2.36	2.32
$a_1 : a_2$	1.001	1.001	0.9907	1.000	0.9807	1.002	0.9892	0.9735
$2V$	0°	2°	6°	0°	8°	3°	8°	10°

A: Burma B: Omiya-chô (Morimoto)
C: Hagata-mura D: Mineyama-chô (Oro)
E: Omiya-chô (Kôbe) F: Yamaguchi-mura
G: Ishikawa-chô H: Otsu-shi (Shimotanakami)

sections measurement of $2V$-values was carried out. $2V$-values were somewhat varied with different portions even in a section. Therefore, the measurement was carried out with ten to fifteen portions in each section. In Table 3 are shown the average $2V$-values of the specimens. Comparing the $2V$-values with $a_1 : a_2$ ratios, it is found that the $2V$-value increases with increasing ratio of $a_1 : a_2$.

Consideration

As the peak in the diffraction pattern is considered to be a sort of distribution curve, though it is not the case in the strict sense, the maxima of the peaks in the diffraction pattern can, therefore, be treated as equivalent to the modes of the distribution curves. In the normal distribution curve the mode is the mean value. Accordingly, cell-dimensions obtained in the present examination represent the mean values of the cell-dimensions of portions in a specimen. Consequently, comparing of the ratios of a_1, : a_2 with average $2V$-values will be reasonable.

The increase of the $2V$-value with increasing ratio of a_1 : a_2 indicates that the biaxial zircon arose from the normal zircon through the anisotropic lattice expansion due to the metamictization. HURLEY and FAIRBAIRN[14] (1953) reported that the diffraction angle of 112 reflexion in zircon decreased with increasing total alpha irradiation. HOLLAND and GOTTFRIED[15] (1955) reported that cell-dimensions of zircon increased as the metamictization went on, however, their calculation was based on the erroneous assumption that the increase in the direction perpendicular to c-axis was isotropic.

The author proposes to give a term *biaxialization* to the phenomenon that uniaxial crystals are transformed into biaxial ones.

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