Acta Cryst. (1955). 8, 291

The Effect of Nuclear Radiation on the Structure of Zircon*

By Heinrich D. Holland
Department of Geology, Princeton University, Princeton, N.J., U.S.A.
and David Gottfried
U.S. Geological Survey, Washington, D.C., U.S.A.

(*Received* 17 *September* 1954 *and in revised form* 27 *October* 1954)

The effect of nuclear radiation from the decay of uranium, thorium and their daughter elements on the specific gravity, unit-cell dimensions, and optical properties of zircon has been studied. During the course of the irradiation the specific gravity of zircon drops 16%, the material becomes isotropic and so disordered as to fail to yield recognizable X-ray diffraction peaks. It is proposed that the observed effects are predominantly due to the displacement of atoms by recoil nuclei and by high temperatures generated in the path of nuclear particles. The breakdown of the structure is envisaged as a four-stage process in which the structure is first saturated with displacements; the saturated structure then breaks down into crystallites of ordered zircon which ultimately break down into a glass.

1. Introduction

It has long been recognized (Damour, 1864) that zircons from different localities show a considerable range of physical properties, and that these variations cannot be explained in terms of differences in chemical composition. In early attempts to systematize the observed variations (Stevanovic, 1903) crystals with chemical composition close to that of pure $ZrSiO_4$ were subdivided into three groups on the basis of optical properties and specific gravity. A further distinction was made between these zircons and those which had been hydrated and altered chemically to an appreciable extent. In 1914 Hamberg (1914) suggested that a genetic relationship exists between the three groups of constant composition, and that the differences in the physical properties of these materials are due to the effects of irradiation by α particles originating in the decay of the radioisotopes of the uranium and thorium series present within the crystal structure. In the 1930's the work of investigators in Germany (Bauer, 1939; Chudoba & Stackelberg, 1936; Stackelberg & Chudoba, 1937; Stackelberg & Rottenbach, 1939*a*, *b*; Lietz, 1937) and England (Anderson & Payne, 1937) confirmed this theory. Anderson & Payne showed that a grouping of zircons according to their specific gravity or optical properties was not justified since samples with properties intermediate between those of the supposed types were common. The work of Chudoba, Stackelberg, and Rottenbach established that the decrease in density, refractive indices and birefringence can be correlated with a breakdown of the crystal structure, as shown by a study of X-ray diffraction patterns. Furthermore, it was shown that in a set of zircons of the same geologic age those containing a high concentration of uranium and thorium showed a greater destruction of the structure than those containing only small amounts of these elements. These observations suggested that nuclear radiation is the cause of the observed changes in the physical properties of zircon. However, an experiment by Stackelberg & Rottenbach (1939*b*) designed to test this effect directly, in which a thin slab of zircon was bombarded by α particles, proved to be inconclusive. The literature has been reviewed recently by Pabst (1952).

A few years ago it was suggested (Holland & Kulp, 1950) that radiation damage in minerals can be used as a means for determining their geologic age. Since then this technique has been applied to some complex oxides (Kulp, Volchok & Holland, 1952), and the validity of the approach has been established. Hurley & Fairbairn (1953) have explored the possibility of using the change in the reflection angle from the {112} planes of zircon as the basis for a similar technique. In the present work an attempt has been made to interpret structurally the observed changes in the physical properties of zircons during irradiation, to establish the nature of the damaging processes, and to explore the applicability of radiation-damage measurements in zircon as a method of age determination. This paper is a summary of the results bearing on the first two of the above problems. The junior author carried out the measurements of the optical properties and determined the age of the Ceylon zircons. The senior author is responsible for the remainder of the experimental work and for the section of this paper dealing with the theory of radiation damage.

---

* Publication authorized by the Director, U.S. Geological Survey.

Most of the observations were made on a set of gem zircons from Ceylon. These had been cut and showed almost no flaws. The remainder of the observations were made on zircons from pegmatites and granites. The latter were separated from the other constituents of the rocks with the use of heavy liquids and a Frantz magnetic separator.

2. Measurement of radiation dosage

The zircon samples had been subjected since their formation to radiation from the radioactive disintegration of uranium, thorium, and their decay products. The total radiation dosage consists of the contribution from α, β, and γ rays as well as from recoil nuclei produced during radioactive decay, a small contribution due to spontaneous fission, and nuclear radiation originating in materials surrounding the crystal in its natural setting. As the uranium and thorium content of zircon is usually much greater than that of the surrounding minerals, the contribution of the latter of these can be neglected. As a measure of radiation dosage due to the decay of uranium, thorium and their daughter elements within the structure, the total number of α disintegrations per mg. was chosen. It can be shown that the total number of α disintegrations per mg., D, is related to the uranium and thorium content and the age of the mineral by the equation

$$D = \bar{\alpha}\,\frac{8(e^{\lambda_{\mathrm{U}}t}-1)+\frac{7}{139}(e^{\lambda_{\mathrm{AcU}}t}-1)+6\varphi(e^{\lambda_{\mathrm{Th}}t}-1)}{8\lambda_{\mathrm{U}}+\frac{7}{139}\lambda_{\mathrm{AcU}}+6\varphi\lambda_{\mathrm{Th}}}, \quad (1)$$

where

D = total number of α disintegrations per mg. of sample since the time of formation,
$\bar{\alpha}$ = present α activity in α's per mg. per year,
λ_{U}, λ_{AcU}, and λ_{Th} = the decay constant in years^{-1} of U^{238}, U^{235}, and Th^{232} respectively,
t = age of sample in years,
φ = present ratio of the number of Th^{232} atoms to the number of U^{238} atoms in the sample.

The error introduced by assuming that equilibrium has obtained in the uranium and thorium decay series since the formation of the samples is small provided that the age, t, of the materials studied is considerably greater than the time required for the establishment of equilibrium in the decay series. This was the case in all of the samples which were studied. Since these crystals were completely unaltered, it appears unlikely that any changes in the composition of the crystals, other than those due to radioactive decay, have occurred within them. Therefore N_{α} can be calculated from the present α activity provided t, the age of the crystals, and the Th/U ratio within them are known. The age t has been determined for a number of the Ceylon crystals by measuring the present α activity and the lead content of the crystals (Gottfried, Senftle & Waring, manuscript report). The results indicate that the crystals are 570±20 million years old. This is in satisfactory agreement with the results of an age determination on a Ceylon zircon by Tilton (personal communication, 1954) in which the concentration of the lead isotopes was determined by an isotope dilution technique, and which yielded a probable age of 560±20 million years. The U/Th ratio in the Ceylon zircon analyzed by Tilton is 9; it appears certain that the U/Th ratio is generally high in all of the Ceylon zircons since the measured uranium content is sufficient to account for the observed α activity of the samples (Gottfried *et al.*, manuscript report; P. M. Hurley, personal communication, September 1954). The U/Th ratio in materials other than those from Ceylon was determined approximately from the ratio of the β–γ to the α activity of the sample, as discussed below.

The α activity of the samples was determined in a scintillation counter using an R.C.A. 5819 photomultiplier tube and housing as described elsewhere (Kulp, Holland & Volchok, 1952). The samples were prepared by crushing in a steel mortar, sieving, weighing out 100 mg. of zircon of grain size between 80 and 200 mesh and introducing the sample into the sample well. It was found that this sample-preparation technique was rapid and that a redetermination of the count rate after reintroduction of the sample into the holder always deviated less than 1·5% from the first value. Differences in grain-size distribution were found to cause errors smaller than this. Counting was continued for all samples until the probable statistical counting error was less than 1%.

The β–γ activity was determined with a standard Geiger counter. The samples were transferred from the α counter to the sample holder of the Geiger counter, an aluminum foil was interposed between sample and Geiger tube to stop α radiation, and counting was usually continued until the statistical counting error was less than 1%. This was not feasible for some samples as the background count rate of approximately 580 counts per hour at times greatly exceeded the count rate due to the zircon sample. The overall reproducibility of the measurements was about 3%.

In order to check possible drifts in the sensitivity of the counters the count rate of every fifteenth sample analysed during the course of the experiments was redetermined at the conclusion of the experiments. No detectable sensitivity drifts were found in either the α or β–γ counters.

As the counters did not determine the absolute α and β–γ activity of the samples, calibration was necessary. This was accomplished by exchanging samples with D. Gottfried (Gottfried, in process) and P. M. Hurley (Hurley & Fairbairn, 1953). There was satisfactory agreement between the calibration factors derived from the two laboratories.

3. Measurement of the density

The density of the Ceylon material was determined by an immersion method, using toluene as the immersion medium. Whole stones were weighed in air and in toluene on a standard analytical balance, and fragments of zircon were similarly weighed on a Berman density balance. The density of the toluene was determined by means of a Christian Becker chainomatic density balance.

Fig. 1 is a plot of the density of the Ceylon zircons as a function of their α activity. The additional scale shows the total number of α disintegrations per mg. of sample calculated on the basis of an age of 570×10^6 years. It can be seen that the density drops at first slowly, then more rapidly, and finally approaches asymptotically a value of approximately 3·96 g.cm.$^{-3}$ at radiation dosages in excess of $1{\cdot}2 \times 10^{16}$ α disintegrations per mg. Since the ratio of the α to the β–γ activity in the Ceylon samples is quite constant, the shape of the curve of density versus β–γ activity is identical to that of Fig. 1.

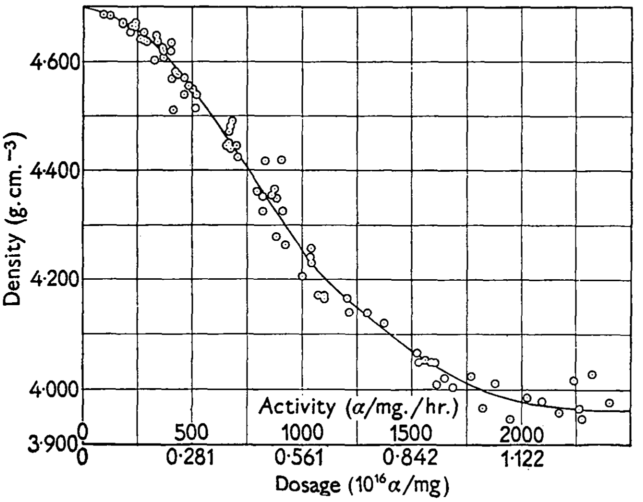


Fig. 1. Density of Ceylon zircons as a function of the present α activity and total α dosage.

4. Measurement of the unit-cell dimensions

The unit-cell dimensions of the zircons were measured with a Norelco high-angle X-ray spectrometer. Silicon metal was used as an internal standard. Because it was desirable to measure the unit-cell dimensions to approximately 1·5 parts per 10,000, a new sample-mounting technique, based on the principle of simultaneous sedimentation of sample and standard, was developed (Holland *et al.*, in course of publication).

Fig. 2 shows the observed variation of c_0 and a_0 of the Ceylon materials as a function of α activity and α dosage. In the first stages of the irradiation the shape of the {101}, {200}, and {112} peaks, which were used to calculate the unit-cell dimension, does not change measurably. However, after the α dosage exceeds $0{\cdot}2 \times 10^{16}$ α/mg. there is a rapid broadening of the peaks (Fig. 3). In particular there is a pronounced skewing of the peaks toward higher values of 2θ. At still greater dosages the skewing is seen to be due to reflection maxima at the 2θ values of undamaged zircon, and the ratio of the height of the second to the height of the first peaks increases markedly. At still higher radiation dosages the first peaks apparently are absent, and in zircons which have suffered irradiation in excess of $1{\cdot}1 \times 10^{16}$ α/mg. the second peaks have also disappeared almost completely. As can be seen from Fig. 2, the unit-cell dimensions of that portion of the crystal giving rise to the first peaks approach a maximum value. The unit-cell dimensions of that portion of the structure giving rise to the second peaks stay essentially constant throughout the range of radiation dosage during which it was observed. There is some uncertainty about the position of the first peaks at high radiation dosages since their position was difficult to measure accurately; similarly the position of the second peaks is uncertain

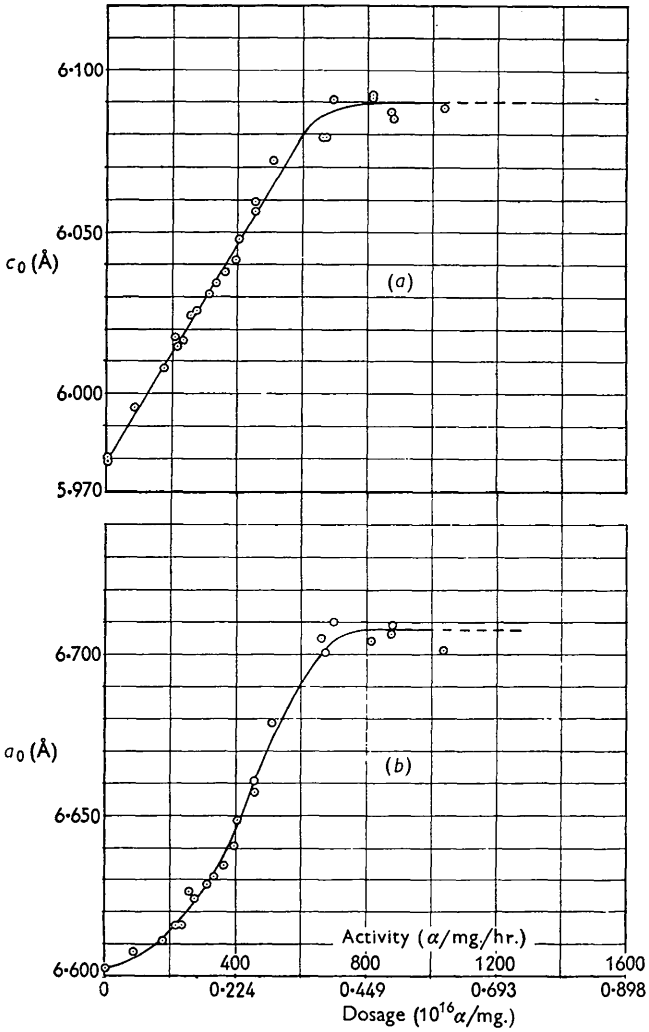
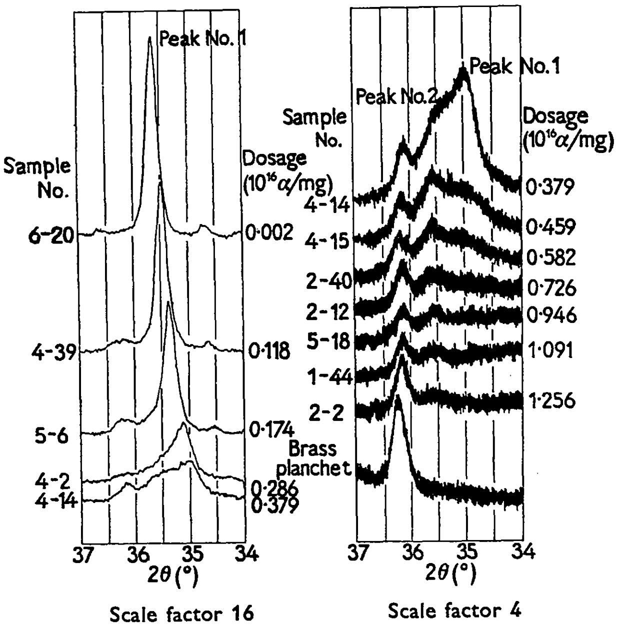


Fig. 2. c_0 and a_0 for Ceylon zircon as a function of the present α activity and total α dosage.



Scale factor 16 Scale factor 4

Fig. 3. The reflection of X-rays from the {112} planes of Ceylon zircon in various stages of disintegration. Cu radiation, no filter; 35 kV., 15 mA.; slits: 4°, 0·006 in., 4°.

at low radiation dosages, as can be seen from Fig. 3.

In Fig. 4, a_0 has been plotted as a function of c_0. Fig. 5 shows the left-hand portion of Fig. 4 and the data for a number of zircons from other localities. It can be seen that the Ceylon data are self-consistent, but that there is considerable variation in the relationship of a_0 and c_0 for zircons as a whole. This discrepancy could be due to differences in the unit-cell dimensions of undamaged zircons from different localities caused by slight differences in the chemical composition of the specimens, due to differences in the behavior of different zircons to the same type of radiation, due to differences in the thermal history of the material since its formation or due to a combination of these factors. On the basis of a number of experiments (Holland, in preparation) it is probable that the last of these explanations is correct; it appears that the Ceylon zircons have suffered slight thermal annealing since their formation, during which the a_0 dimension of material which was slightly damaged has been affected.

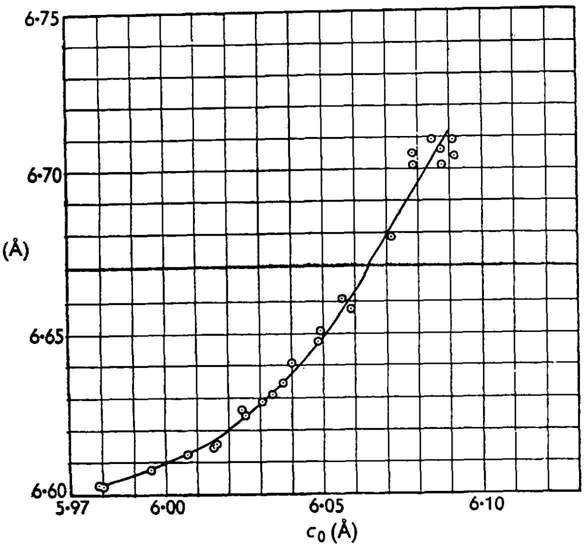


Fig. 4. a_0 as a function of c_0 for Ceylon zircon.

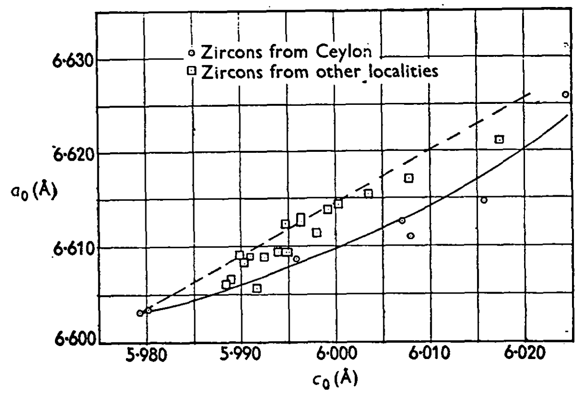


Fig. 5. Comparison of the relationship of a_0 to c_0 in Ceylon zircons and in those from other localities.

5. Measurement of optical properties

The two indices of refraction of a number of the Ceylon specimens were determined by an immersion technique. The results are shown in Fig. 6, in which the two refractive indices have been plotted as a function of the present α activity and of the α dosage. The index/dosage curves are initially flat, a phenomenon which has also been observed for a large number of zircons from other localities. When the dosage exceeds $0{\cdot}15 \times 10^{16}$ α/mg. the curves drop sharply and approach an index of 1·810 asymptotically.

6. Interpretation of the data

The X-ray data afford the best qualitative approach to a structural interpretation of the above observations. The change in the nature of the Bragg reflections can be summarized in terms of the following steps:

(1) Shifting of the peaks to lower reflection angles without appreciable change in peak shape.
(2) Decrease of peak height and skewing towards the direction of higher values of 2θ.
(3) Definite appearance of the second peaks, and rapid disappearance of peaks No. 1.
(4) Reduction of the height of peaks No. 2 and complete disappearance of peaks No. 1.
(5) Almost complete disappearance of peaks No. 2.

In order to interpret step (1) of the irradiation response it is first necessary to consider the possible effects of the nuclear radiation available for damaging the structure. These can be grouped under ionization

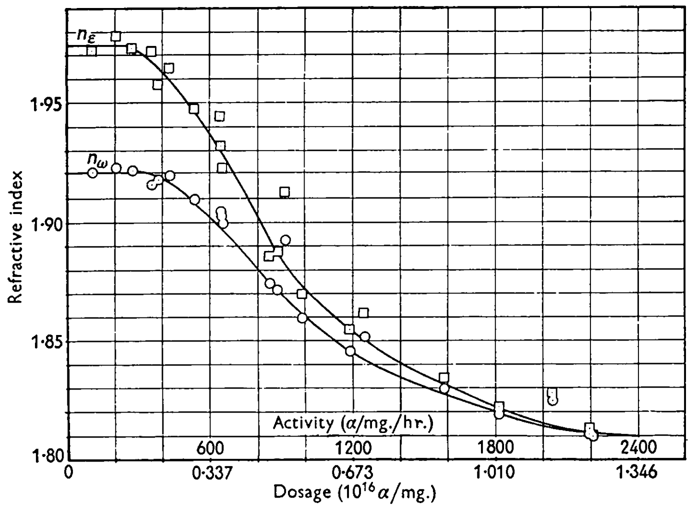


Fig. 6. The indices of refraction of Ceylon zircon as a function of their present α activity and total α dosage.

and displacement of atoms (Dienes, 1953). The former is accomplished mainly by α, β and γ radiation, the latter mainly by the effect of recoil nuclei and α particles (Seitz, 1949). Displacement of atoms will certainly contribute towards a disordering of the structure. Therefore, if it can be shown that such displacements are sufficient in number to produce the observed effects, it can be concluded that ionization phenomena play only a minor role in the disruption of the structure. Conversely, if it can be shown that displacement phenomena can account for only a small fraction of the observed effects, ionization processes probably are mainly responsible for the major portion of the structure damage. The energy of a uranium recoil nucleus after α emission is approximately 70,000 e.V. On the basis of work by Murray & Taylor (1954) it is probable that several hundred displacements are produced by such a particle. Seitz (1949) has shown that approximately 50 displacements might be expected at the end of each α track. Thus about 500 displacements should be produced in the structure during α emission. It was shown above that the structure is completely destroyed after approximately $1{\cdot}2\times10^{16}$ α disintegrations per mg. have occurred. There are $1{\cdot}95\times10^{19}$ atoms per mg. of zircon, so that after a dosage of $1{\cdot}2\times10^{16}$ α/mg. approximately 30% of the atoms in the structure have been displaced owing to collisions with recoil nuclei and α particles. It is probable that this number of displacements would suffice to destroy the structure, provided that at earth-surface temperatures self-annealing is slow compared to the rate of damage. That this is so is indicated by the fact that a given dosage has produced the same damage in specimens ranging in age from 300×10^6 to 1200×10^6 years (Holland, in preparation). From this it appears probable that the major part of the damage is caused by direct displacements, and that these are predominantly caused by recoil nuclei.

It is next of interest to inquire whether these displacements are clustered in the structure or whether a fairly even distribution is present during the first stages of disintegration. If clusters of highly disordered material of a glassy nature were present it might be expected that the X-ray reflections would become skewed immediately, and that there would initially be very little shift of the position of the peaks; that this is not the case has been indicated above. On the other hand, a homogeneous distribution of displacements would be expected to produce a general distension of the structure, as has been pointed out by Tucker & Sampson (1954). It therefore seems likely that in the first stage of disintegration the distribution of displacements is relatively uniform throughout the crystal.

Steps (2) and (3) of the irradiation history are characterized by a general flattening of the curves of c_0 and a_0 versus dosage, by the appearance of the second peaks and by the decrease of the height of peaks No. 1. The flattening of the curves of c_0 and a_0 versus dosage indicates that phase No. 1 has expanded to its maximum dimensions. The appearance of peaks No. 2 indicates that a portion of the sample is essentially free of displacements. This portion might consist of a fraction of the sample in which the concentration of the radio-elements is much lower than in the remainder of the crystal, and in which, therefore, the rate of damage is considerably slower than in the remainder of the sample. If this were the correct interpretation, the apparent growth of peaks No. 2 would be due to the combined effect of the shift of peaks No. 1 and the attendant decrease in the amplitude. Such an explanation, based on the inhomogeneity of the sample, would lead one to predict the presence of various degrees of inhomogeneity in different zircon samples. This, in turn, would result in a variability of peak shapes at a given level of radiation dosage. Since no appreciable variability was found, it is improbable that the appearance of peaks No. 2 can be ascribed to inhomogeneity of the sample. Further evidence of the considerable homogeneity of the samples is supplied by the smallness of the differences between the values of the specific gravity of different fragments of the same Ceylon zircon (Table 1). Since the peaks No. 2 are, therefore, probably not residual, they are apparently due to a new phase. This new phase reacts differently to nuclear radiation in that there is no noticeable shift in 2θ value of the X-ray reflections prior to and during the disappearance of the phase. On the basis of the X-ray data it is difficult to decide at which stage in the irradiation Phase 2 is first present. The first evidence of the presence of Phase 2 is the slight broadening in zircon 5-6 of the {112} reflection, which is then obviously present in zircon 4-2.

Table 1. *Comparison of the specific gravity of the fragments of some Ceylon zircons**

Zircon No.	Fragment No. 1	2	3	4	5
3	3·996	4·002	4·004	—	—
And. 1	4·190	4·213	4·191	4·199	4·167
5	4·351	4·353	4·373	—	—
2-28	4·377	4·372	4·351	4·346	4·345
3-1	4·430	4·437	4·424	4·396	—
2-32	4·548	4·537	4·552	4·537	—
4-6	4·575	4·630	4·555	4·581	—

* These determinations were made with a Berman density balance; toluene was used as the immersion medium. The fragments weighed between 25 and 50 mg. Duplicate determinations on the same fragment usually differed by less than 0·010.

It can, furthermore, be shown that a third phase of low density must appear during this stage of irradiation. In Fig. 7 the reciprocal of the unit-cell volume calculated for Phase 1 is plotted against the measured density of the stones. Initially all the points fall on a straight line, the slope of which is the mass present in the unit cell. The molecular weight calculated on the basis of this slope is 184·7; this corresponds to the value for $ZrSiO_4$ containing as the major impurity 1% Hf, which is close to the average hafnium content of fifteen Ceylon zircons, as shown in Table 2 (Waring & Worthing, manuscript report). At a dosage of $0{\cdot}3\times10^{16}$ α/mg. the experimental curve in Fig. 7 begins to deviate from the straight-line relationship maintained earlier. In this range Phase 2, giving rise to peaks No. 2, is present. Since $1/V$ for this phase is equivalent to that for undamaged zircon, a third phase must be present of density sufficiently low so that the combined $1/V$ of the three phases falls on the initial straight line. Since the third phase does not give an X-ray pattern, it is presumably so disordered as to deserve to be called a glass, which will be called Phase 3.

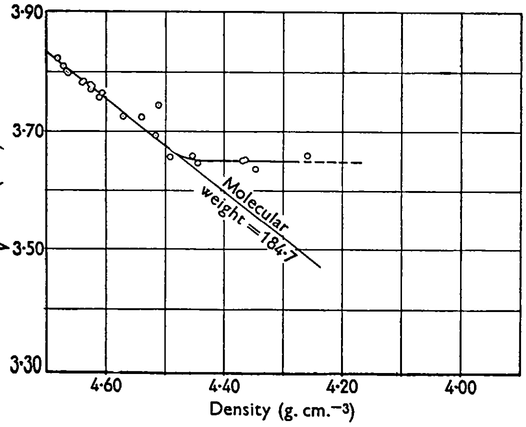


Fig. 7. The reciprocal of the unit-cell volume ($1/V$) of Phase 1 plotted against the density of the sample.

Table 2. *The relationship of the α activity and hafnium content in some Ceylon zircons*

Sample No.	Activity (α/mg./hr.)	Hf (%)
1	103	0·55
4-33	150	0·66
2	273	0·78
3-16	352	0·38
3	643	0·56
4	882	1·7
2-18	913	1·4
2-23	985	1·25
6	1185	1·4
2-17	1245	1·16
7	1583	1·8
9	1815	0·71
1-2	2040	1·6
10	2197	1·8
1-26	2210	1·3
	Average	1·14

On the basis of the X-ray data, Phases 2 and 3 both increase in amount during step (3); then, as the intensity of the peaks No. 2 falls off again together with those of Phase 1, the proportion of Phase 3 continues to increase. Ultimately both Phases 1 and 2 disappear and Phase 3 comprises all of the structure.

On the basis of the data on the optical properties, density and unit-cell dimensions, it is possible to determine quantitatively the changes of the concentration of the three phases within the material. The ordinary and extraordinary index of refraction of a zircon crystal can be shown to consist of three terms:

$$n_\omega = f_1 n_{\omega1}+f_2 n_{\omega2}+f_3 n_3 , \tag{2}$$

$$n_\varepsilon = f_1 n_{\varepsilon1}+f_2 n_{\varepsilon2}+f_3 n_3 , \tag{3}$$

where

f_1 = fraction of Phase 1 in the crystal,
f_2 = fraction of Phase 2 in the crystal,
f_3 = fraction of Phase 3 in the crystal,
n_ω = ordinary index of crystal,
n_ε = extraordinary index of crystal,
$n_{\omega1}$ = ordinary index of Phase 1,
$n_{\varepsilon1}$ = extraordinary index of Phase 1,
$n_{\omega2}$ = contribution of Phase 2 to the ordinary index of the crystal,

$n_{\varepsilon 2}$ = contribution of Phase 2 to the extraordinary index of the crystal,
n_3 = index of Phase 3.

f_1, f_2, and f_3 are related by the equation

$$f_1+f_2+f_3 = 1\,. \tag{4}$$

The ordinary and extraordinary indices, n_ω and n_ε, can be measured directly. As can be seen from Fig. 6, there is no change in the refractive indices of zircons during the initial stages of irradiation. As f_2 and f_3 are essentially equal to zero in this dosage range it follows that $n_{\omega 1}$ and $n_{\varepsilon 1}$ are essentially independent of radiation dosage, which is to be expected if the effect of the increase in the average polarizability of the ions due to the disordering effect of the nuclear radiation is just balanced by the decrease in specific gravity accompanying this disorder. The refractive indices for undisturbed material can therefore be used with sufficient accuracy for $n_{\omega 1}$ and $n_{\varepsilon 1}$. As Phase 2 consists of zircon containing very few displacements, the ordinary and extraordinary indices of this phase are equal to those of undisturbed zircon. It can be shown from the optical and X-ray data that Phase 2 consists of small crystals which are not aligned with the residual structure due to Phase 1. It cannot be said how complete the disorder actually is; in the present calculation the assumption of complete randomness is made, which will be justified below. It follows that $n_{\omega 2} = n_{\varepsilon 2} = n_2'$. This can be calculated either by taking an average of n_ω and n_ε of the form

$$n_2' = \tfrac{1}{3}(2n_\omega+n_\varepsilon)$$

or of the form

$$n_2' = (n_\omega^2 n_\varepsilon)^{\frac{1}{3}}\,.$$

In each case the same value, 1·939, results; thus considerable confidence can be placed in the value assigned to n_2'.

As Phase 3 is apparently a ZrSiO$_4$ glass, and as this is the final state of the material after complete disruption of the structure, n_3 can be set equal to 1·810.

Equations (2), (3) and (4) can now be solved for f_1, f_2 and f_3. The results are shown in Fig. 8. It can be seen that the trends of the three curves agree with the shapes predicted on the basis of the X-ray diffraction data. A check on the validity of these curves can be obtained if Anderson & Payne's (1937) data are included in the calculations. Since their data are related to the density rather than to the α activity of the Ceylon zircons, Fig. 9 shows f_1, f_2 and f_3 from the data of Gottfried, and of Anderson & Payne plotted as a function of the density. The agreement between the two sets of data is satisfactory.

Another check on the correctness of the curves of Fig. 8 can be obtained by combining the density measurements with those of the unit-cell dimensions. It can be shown readily that the density, ϱ, and the densities ϱ_1, ϱ_2 and ϱ_3 of Phases 1, 2 and 3 respectively are related by the equation

$$\frac{1}{\varrho} = \frac{f_1}{\varrho_1}+\frac{f_2}{\varrho_2}+\frac{f_3}{\varrho_3}\,. \tag{5}$$

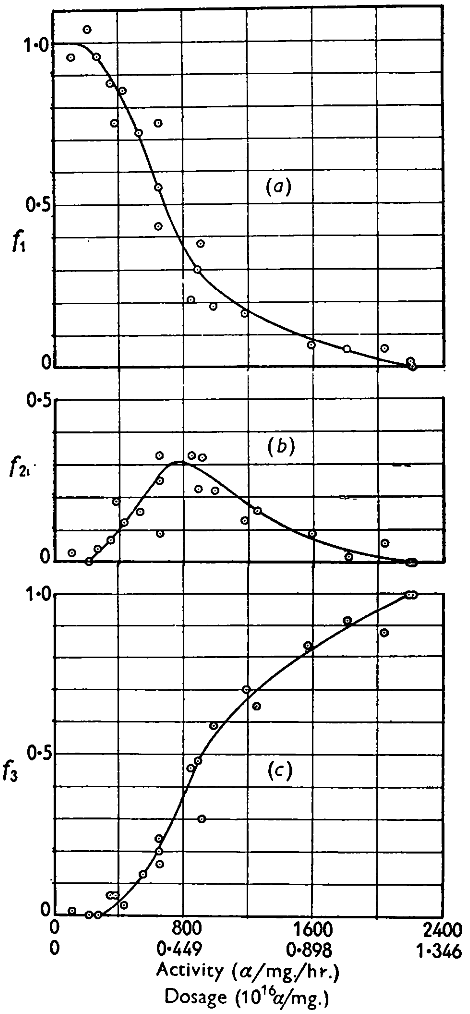


Fig. 8. The fractions of Phases 1–3 (f_1, f_2 and f_3) as a function of α dosage.

The density ϱ is determined directly, ϱ_1 is calculated from the unit-cell dimensions of Phase 1, ϱ_2 is the density of undamaged zircon, and ϱ_3, the density of zircon glass, is assumed to be equal to that of the stones as a whole after the structure has been completely destroyed.

This equation and the relation (4) are not sufficient in themselves to permit a solution for f_1, f_2 and f_3. The data on relative peak heights and peak areas are not sufficiently accurate to be used in this connection. It is therefore necessary to use one of the relationships derived above from the optical data to permit the solution of the above equation for the desired quantities. In Fig. 10 f_2 and f_3, calculated in this manner,

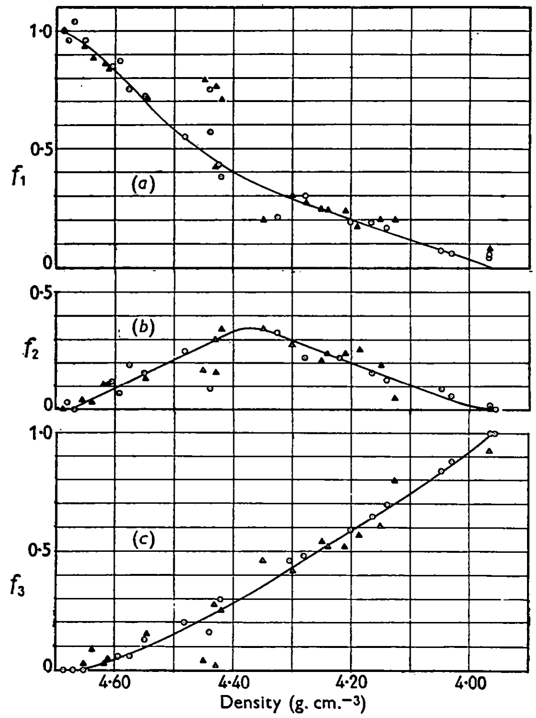


Fig. 9. The fractions of Phases 1–3 (f_1, f_2 and f_3) as a function of density. Circles: Gottfried; triangles: Anderson & Payne.

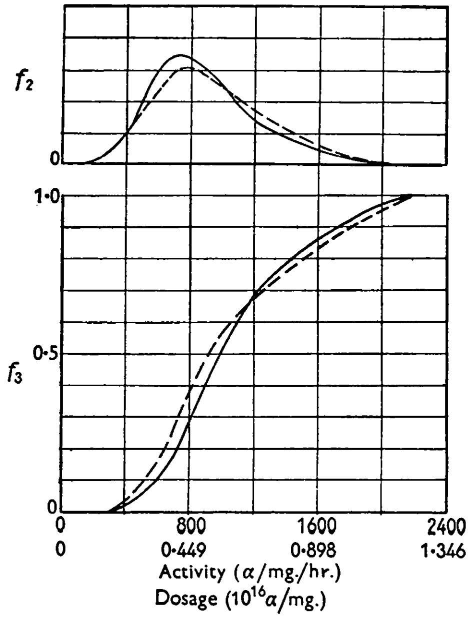


Fig. 10. The fractions of Phases 2 and 3 (f_2 and f_3), as calculated on the basis of optical data (broken line) and on the basis of density data (full line), plotted as a function of α dosage.

have been plotted as functions of the radiation dosage. It can be seen that the two curves check well with the curves derived from the optical data alone, and lend support to the interpretation of the data which is here proposed.

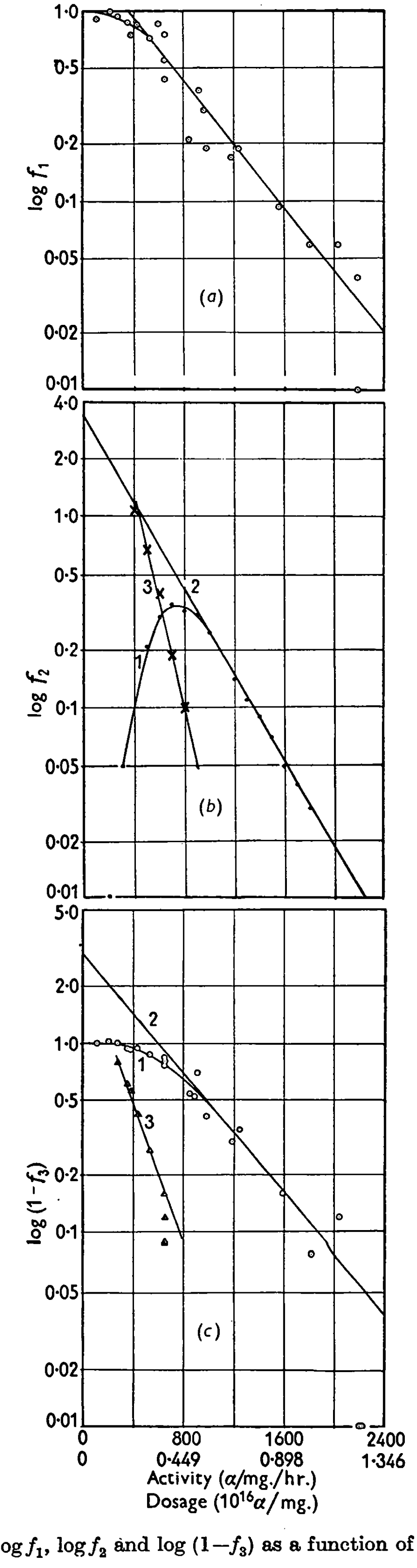


Fig. 11. log f_1, log f_2 and log $(1-f_3)$ as a function of α dosage.

Finally it is of interest to attempt a kinetic interpretation of the curves of f_1, f_2 and f_3 as functions of the dosage. In the initial stages of irradiation f_1 stays constant, because the structure is merely being saturated with displacements. In Fig. 11(*a*), $\log f_1$ has been plotted as a function of the dosage. It is apparent that an equation of the type

$$f_1 = \exp\left[-k_1(D-D_0)\right], \tag{6}$$

where D_0 is the dosage at which breakdown begins, adequately describes the decay of f_1. The greatest discrepancy occurs at low values of the dosage. This is to be expected since a sudden appearance of Phase 2 at $D = D_0$ in accord with equation (6) would be prohibited by the necessarily somewhat uneven distribution of displacements within the structure during the course of irradiation. In the most general case Phase 1 might be expected to break down into Phases 2 and 3. Similarly Phase 2 might be expected to become saturated with displacements (and thus be considered part of Phase 1 again) and then break down into Phase 2 and 3. Finally there might be some annealing of Phase 3, so that either Phase 2 or Phase 1 is regenerated in some form from Phase 3. The X-ray data, however, indicate that Phase 2 decays directly into Phase 3 without prior expansion since there is apparently no shift of the Phase 2 peaks to lower 2θ values such as is observed in the breakdown of Phase 1. Furthermore, Phase 3 does not appear to anneal back appreciably either to Phase 1 or to Phase 2 since in the most highly irradiated samples the peaks due to Phase 1 are completely absent and those due to Phase 2 are barely discernible. The decay scheme may therefore be diagrammed in the form

$$\begin{tikzcd}(1) \arrow[r] & (2) \arrow[d] & + & (3) \\ & (3) & & \end{tikzcd}$$

Assuming a first-order reaction such as has been shown to be valid for the decay of f_1, we can write

$$\frac{df_2}{dD} = k_2k_1 \exp\left[-k_1(D-D_0)\right]-k_3f_2\,, \tag{7}$$

$$\frac{df_3}{dD} = (1-k_2)k_1 \exp\left[-k_1(D-D_0)\right]+k_3f_2\,, \tag{8}$$

from which it follows that

$$f_2 = \frac{k_2k_1}{k_3-k_1}\left[\exp\left[-k_1(D-D_0)\right]-\exp\left[-k_3(D-D_0)\right]\right], \tag{9}$$

$$f_3 = 1-\left[1+\frac{k_2k_1}{k_3-k_1}\right]\exp\left[-k_1(D-D_0)\right] + \frac{k_2k_1}{k_3-k_1}\exp\left[-k_3(D-D_0)\right]. \tag{10}$$

In Fig. 11(*b*) f_2 has been plotted as a function of dosage (black circles). The line 2 represents the contribution of the first exponential term, and the line 3, defined by the difference between the value of f_2 and the intercept of line 2, represents the contribution to f_2 of the second exponential term. In Fig. 11(*c*) $\log(1-f_3)$ has been plotted as a function of D. It can be seen that $(1-f_3)$ is also the sum of two exponentials. By an analysis of the curves of f_1, f_2 and f_3 as functions of the dosage the constants k_1, k_2 and k_3 can be found. These are shown in Table 3. It is of interest that k_2 does not differ from unity by more than the experimental limit of error, so that finally the decay scheme reduces to the form

$$(1) \rightarrow (2) \rightarrow (3)\,.$$

Table 3. *Values of* k_1, k_2, k_3 *and* D_0 *in equations* (6), (9) *and* (10)

Source	k_1	k_2	k_3	D_0
Curve of f_1/D	$3{\cdot}4\times10^{-16}$	—	—	$0{\cdot}20\times10^{16}$
Curve of f_2/D	$4{\cdot}6\times10^{-16}$	1·6	$11{\cdot}6\times10^{-16}$	$0{\cdot}25\times10^{16}$
Curve of f_3/D	$3{\cdot}3\times10^{-16}$	0·73	$7{\cdot}7\times10^{-16}$	$0{\cdot}22\times10^{16}$
Average	$3{\cdot}8\times10^{-16}$	1·2	$9{\cdot}6\times10^{-16}$	$0{\cdot}22\times10^{16}$

Structurally this indicates that after a certain concentration of displacements is reached in Phase 1, thermal spikes due to the passage of nuclear particles cause nucleation of undamaged crystals in Phase 1 as has been suggested by Brinkman (1954). It might be expected that these crystals would be small and randomly arranged with respect to the remaining structure. That this is so is corroborated by the fact that Phase 2 then passes directly into glass under the effect of the irradiation, rather than first going through a cycle of expansion.

The numerical values of Table 3 are of some interest. The specific gravity of zircon at a dosage of $0{\cdot}22\times10^{16}$ α/mg. is 4·58, i.e. 2·5% less than that of undamaged zircon. The total drop in specific gravity during the destruction of the structure is 16%; these figures suggest that when approximately 16% of the atoms have been displaced, the structure is saturated with displacements, and nucleation of Phase 2 becomes important. If this figure can be accepted, it follows that in zircon the volume of a displaced atom plus that of a vacancy is on the average 16% greater than the volume originally occupied by the atom in its normal lattice position. Furthermore, if a dosage of $0{\cdot}22\times10^{16}$ α/mg. dislocates 16% of the atoms in the structure, the net number of atoms displaced per α disintegration is approximately 1500.

The values of k_1 and k_3 indicate that 7,600 f_1 atoms are transferred from Phase 1 to Phase 2 and 19,200 f_2 atoms from Phase 2 to Phase 3 per α disintegration after the structure has become saturated with displacements. The large difference between the possible number of atoms transferred from Phase 1 to Phase 2 and from Phase 2 to Phase 3, as compared with the number of atoms displaced per α disintegration in nearly undamaged zircon, suggests that a different mechanism of atomic rearrangement is operative in the different stages of structure damage. It is proposed that direct dislocation by knock-ons be made responsible for the displacement of atoms in essentially undamaged material, that nucleation of crystallites by thermal effects—perhaps in the wake of α particles—causes the breakdown of the structure into crystallites, and that the formation of glass is due to a combination of these factors acting on the zircon crystallites.

The above interpretation may shed light on the puzzling phenomenon that some minerals become damaged readily at dosages at which others show no detectable radiation effects (Primak, 1954). Uraninite, for instance, remains crystalline at dosages far in excess of those required to destroy completely the structure of zircons. It has been proposed that the rate of self-annealing at earth-surface temperatures is particularly high for minerals of the uraninite type. However, it is difficult to see how the rate of self-annealing of uraninite could differ very greatly from that of the rare-earth oxides which are usually found in the metamict state. If the mechanism proposed above for the disintegration of the structure of zircon is applicable generally to the formation of metamict minerals, the critical step in the production of radiation damage may be the breakdown of Phase 1 into Phase 2; for, if Phase 2 is disoriented, as is the case in zircons, the further breakdown to a glass may be accomplished readily. On the other hand, if Phase 2 is aligned with the residual structure, then the crystal goes through a constant process of self-annealing and no appreciable fraction of glass may ever be formed. Whether or not Phase 2 is aligned with the residual structure depends on the degree of remanent structure at the time of breakdown and on the tendency of the crystallites to align themselves with this structure. Both of these factors are structure sensitive, and may be the determining factors in the response of crystals to the type of radiation discussed in this paper.

The authors wish to thank Mr Arthur Riemer and Mr Peter Cartwright for assistance in determining the density of the Ceylon zircons. Mr William B. Head, III, Mr George G. Witter, Jr., Mr David B. Schulz, Mr Manuel N. Bass, and Mr George B. Hess assisted in the determination of unit-cell dimensions. Thanks are also due to Mr Paul Bartholomé for the preparation of pure zircon concentrates. This work was supported by the Office of Naval Research under contract number Nonr 250(00).

Mr Gottfried's contribution to the investigation is part of a program conducted by the U.S. Geological Survey on behalf of the Division of Research of the U.S. Atomic Energy Commission.

References

Anderson, B. W. & Payne, C. J. (1937). *Gemmologist*, **7**, 298.

Bauer, A. (1939). *N. Jb. Min. Geol. Beil.-Bd.* A, **75**, 159.

Brinkman, J. A. (1954). *J. Appl. Phys.* **25**, 961.

Chudoba, K. & Stackelberg, M. v. (1936). *Z. Kristallogr.* **95**, 230.

Damour, C. A. (1864). *C. R. Acad. Sci., Paris*, **58**, 154.

Dienes, G. J. (1953). *Ann. Rev. Nuclear Sci.* **2**, 187.

Hamberg, A. (1914). *Geol. För. Stockh. Förh.* **36**, 31.

Holland, H. D. & Kulp, J. L. (1950). *Science*, **111**, 312.

Hurley, P. M. & Fairbairn, H. W. (1953). *Bull. Geol. Soc. Amer.* **64**, 659.

Kulp, J. L., Holland, H. D. & Volchok, H. L. (1952). *Trans. Amer. Geophys. Un.* **33**, 101.

Kulp, J. L., Volchok, H. L. & Holland, H. D. (1952). *Amer. Min.* **37**, 709.

Lietz, J. (1937). *Z. Kristallogr.* **88**, 201.

Murray, G. T. & Taylor, W. E. (1954). *Acta Metallurg.* **2**, 52.

Pabst, A. (1952). *Amer. Min.* **37**, 137.

Primak, W. (1954). *Phys. Rev.* **95**, 837.

Seitz, F. (1949). *Disc. Faraday Soc.* No. 5, 271.

Stackelberg, M. v. & Chudoba, K. (1937). *Z. Kristallogr.* **97**, 252.

Stackelberg, M. v. & Rottenbach, E. (1939*a*). *Z. Kristallogr.* **102**, 173.

Stackelberg, M. v. & Rottenbach, E. (1939*b*). *Z. Kristallogr.* **102**, 207.

Stevanovic, S. (1903). *Z. Kristallogr.* **37**, 247.

Tucker, C. W. & Sampson, J. B. (1954). *Acta Metallurg.* **2**, 433.