FISSION FRAGMENT DAMAGE IN ZIRCONIA

M. C. Wittels and F. A. Sherrill
Solid State Division, Oak Ridge National Laboratory,* Oak Ridge, Tennessee
(Received May 6, 1959)

Natural monoclinic ZrO_2 was reported[1] to transform into the high-temperature cubic modification upon exposure to fast neutrons. In that same study it was suggested that thermal spikes contributed to the transition by means of a rapid high-temperature quench. Further efforts to study these effects in synthetic single crystals and powders of ZrO_2 have proved unsuccessful because the transition could not be effected even with irradiation doses higher by a factor of four over the original irradiation dosage. This is demonstrated in the single-crystal x-ray diffraction pattern in Fig. 1.

Unirradiated portions of the original natural material were subjected to neutron activation analysis in order to determine the concentration of natural uranium and thorium which these oxides often contain as impurities. As expected, it was found that the material which undergoes a phase transition upon fast neutron irradiation contains uranium and thorium in concentrations of 3550 ppm and 39.2 ppm, respectively. As will be shown later, the number of fission events which took place in this material upon exposure to 9.4×10^{19} neutrons/cm^2 was of sufficient magnitude to completely transform the monoclinic structure into the high-temperature cubic phase. It is apparent, also, that the monoclinic ZrO_2 is stable under fast-neutron bombardment, contrary to earlier beliefs,[1] and that the observed irradiation-induced phase transition is produced by the action of fission fragments. As a result of these findings further experimental evidence is available to support proposals of a "fission spike" mechanism.[2-5]

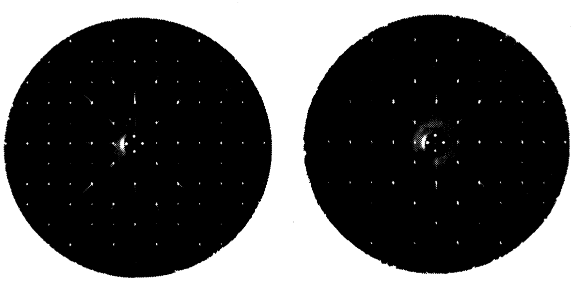


FIG. 1. Zero level precession photographs—(*HK*0) projection (*a*) Before irradiation; (*b*) After irradiation with $3.6 \times 10^{20} nvt_f$.

Samples of ZrO_2 with known concentrations of fissionable impurities were subjected to thermal neutron dosages at irradiation levels capable of producing partial transformation from the monoclinic to the cubic structure. Since these fissionable atoms were contained within the crystal lattice of ZrO_2 in amounts less than 0.5% and since the range of a 100-Mev fission fragment is probably less than 8×10^{-4} cm in this material, it is reasonable to assume that (1) nearly all of the fission fragment energy is dissipated within the crystal lattice, and (2) the local areas surrounding each fission event are sufficiently separated to be termed independent regions. Then if there are no annealing-type rearrangements of atoms within the damaged regions a reasonable estimate of the number of atoms affected by a fission fragment can be made by determining the fraction of transformed material in partially transformed crystals. Figure 2 shows some x-ray diffraction patterns from which these estimates are made.

The method used in this analysis was to measure the integrated line intensities of the two phases directly from the Debye-Scherrer photographs. From the relative change in intensities of these lines with increasing irradiation dosage the estimates of percentage transformation were obtained. It is felt that the over-all accuracy of these estimates is within ±25%, the greatest inaccuracy being caused by radioactivity-induced film fogging. Some overlapping of damaged re-

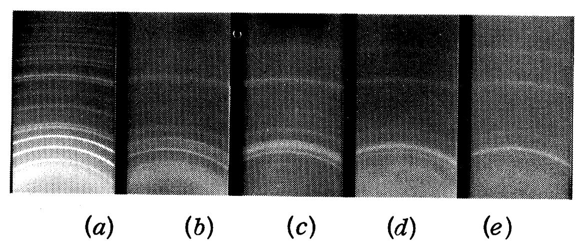


FIG. 2. Debye-Scherrer photographs of ZrO_2 irradiated with fission fragments. (*a*) Before irradiation; (*b*) After irradiation with 7.66×10^{14} fissions per cm^3, 5% transformed; (*c*) After irradiation with 6.67×10^{15} fissions per cm^3, 50% transformed; (*d*) After irradiation with 1.07×10^{16} fissions per cm^3, 80% transformed; (*e*) After irradiation with 3.39×10^{16} fissions per cm^3, completely transformed.

gions probably occurs with dosages in excess of 5×10^{15} fissions per cm^3, so greater accuracy is obtained when less than 50% of the material has been transformed. By this analysis it is seen that $\sim 10^6$ atoms are affected by each fission fragment in inducing the phase transition. In the original observation of the irradiation-induced phase transition,[1] the particle size of the transformed crystallites was ~100A radius as determined from x-ray diffraction line breadths. Particles of this size would contain about 3.5×10^5 atoms, lower by a factor of three from the 10^6 atoms estimated in the present work. The discrepancy is not unreasonable, however, since the x-ray line breadth determination did not consider the strain contribution to the line broadening. If the true particle size was as much as 140A radius, no discrepancy would exist and both cases would give 10^6 atoms affected by each fission fragment. Other irradiation-induced phase transitions in reactor fuel materials[6,7] have been reported, and it is interesting to note that estimates[7] of the number of atoms affected in a U-Mo alloy by a single fission event is fairly close to the number proposed here for the insulator ZrO_2. Calculations using the method of Seitz[8] show that a pair of fission fragments in a material like ZrO_2 would produce about 10^4 displaced atoms as a result of elastic collisions. It does not seem likely that a single displaced atom could affect 200 surrounding atoms to produce a phase transition, and this is supported by the stability of the material under fast neutron bombardment, solely. It is more likely that the process under which the transition occurs is a "fission spike" mechanism with a rapid, high-temperature quench.

The results of this investigation indicate that monoclinic ZrO_2 is stable under fast neutron bombardment but that it transforms into the cubic phase under the action of fission fragments. In this material it appears that $\sim 2 \times 10^6$ atoms are quenched into the high-temperature modification as a result of the energy dissipated by a pair of fission fragments.

---

*Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

[1]M. C. Wittels and F. A. Sherrill, J. Appl. Phys. 27, 643 (1956).

[2]H. Brooks, Knolls Atomic Power Laboratory Report KAPL-360, August, 1950 (unpublished).

[3]J. Ozeroff, Atomic Energy Commission Report AECD-2973, 1949 (unpublished).

[4]J. A. Brinkman, J. Appl. Phys. 25, 961 (1954).

[5]G. H. Kinchin and R. S. Pease, in Reports on Progress in Physics (The Physical Society, London, 1955), Vol. 18, p. 1.

[6]Konobeevsky, Pravdyuk, and Kutaitsev, in Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955 (United Nations, New York, 1956), Paper No. A/Conf. 8P681.

[7]M. L. Bleiberg, in Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958 (United Nations, Geneva, 1959), Paper No. A/Conf. 15P619.

[8]F. Seitz, Discussions Faraday Soc. 5, 271 (1949).

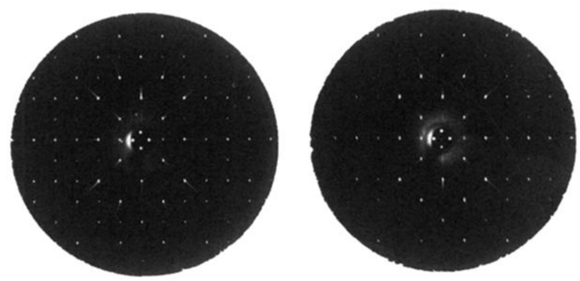
PROTON CAPTURE GAMMA RAYS IN THE GIANT RESONANCE REGION

H. E. Gove, A. E. Litherland, and R. Batchelor*
Atomic Energy of Canada Limited, Chalk River, Ontario, Canada
(Received July 20, 1959)

Measurements of the 90° yield of gamma rays resulting from the capture of protons, with energies up to 11 Mev, in B^{11} and Al^{27} have been made using the Chalk River Tandem Accelerator.[1] In both cases the gamma rays investigated were those leading to the ground and first excited states (4.43 and 1.78 Mev) of the appropriate residual nucleus, C^{12} and Si^{28}, respectively. In addition, the angular distributions of these gamma rays with respect to the incident proton beam were measured at several proton energies. This Letter reports principally the results of the reaction $B^{11}(p,\gamma)C^{12}$ ($Q = 15.949$ Mev).

The gamma rays were detected in a 5-inch diameter by 6-inch long unshielded NaI(Tl) crystal.[2] For the angular distribution measurements a second 5-inch diameter by 4-inch long NaI(Tl) detector was used at a fixed angle as a monitor.

Both the aluminum and boron targets were thin self-supported films through which the beam passed to be stopped in a lead plate behind shielding blocks about 16 feet from the target. The boron targets were prepared by mixing finely powdered boron of normal isotopic abundance with a colloidal graphite suspension in alcohol. This mixture was spread on a glass plate and the



(*a*) (*b*)

FIG. 1. Zero level precession photographs – (*HK*0) projection (*a*) Before irradiation; (*b*) After irradiation with $3.6 \times 10^{20}\, nvt_f$.

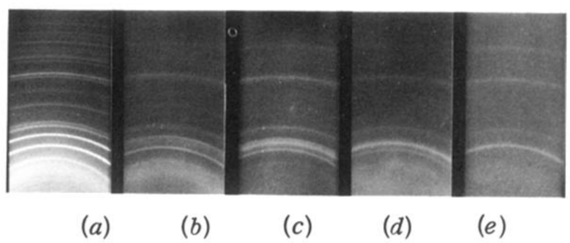


FIG. 2. Debye-Scherrer photographs of ZrO_2 irradiated with fission fragments. (*a*) Before irradiation; (*b*) After irradiation with 7.66×10^{14} fissions per cm^3, 5% transformed; (*c*) After irradiation with 6.67×10^{15} fissions per cm^3, 50% transformed; (*d*) After irradiation with 1.07×10^{16} fissions per cm^3, 80% transformed; (*e*) After irradiation with 3.39×10^{16} fissions per cm^3, completely transformed.