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X-ray Diffuse Scattering from Neutron-Irradiated Uranium Dioxide Crystals

By S. Szarras* and E. M. Hörl

Österreichische Studiengesellschaft für Atomenergie GmbH, Institut für Metallurgie,
Forschungszentrum Seibersdorf, Austria

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The distribution of the diffuse scattering intensity of uranium dioxide single crystals has been studied before and after irradiation by reactor neutrons with doses of 10^{14}, 10^{15} and $5 \, . \, 10^{16}$ fissions cm^{-3}. It has been found that irradiation effects occured only at $5 \, . \, 10^{16}$ fissions cm^{-3}. The $\{002\}_k$ planes of irradiated UO_2 and the $\{22\bar{4}\}_k$ and $\{11\bar{3}\}_k$ planes of unirradiated crystals have been observed as planes of high diffuse intensity. In unirradiated crystals the measured relative intensities around the 335 reciprocal-lattice point are in fair agreement with calculations using the Jahn formula, *i.e.* they have a maximum in the $[33\bar{1}]$ direction. In irradiated samples, however, there exists a weak [002] maximum. This change in the distribution cannot be interpreted by Stokes–Wilson scattering alone and the extra intensity may be explained by the scattering of X-rays from defect modes of lattice vibrations.

Introduction

The knowledge of radiation damage in fissile materials is of great interest for nuclear reactor technology. In particular, irradiation effects in fissile ceramics such as uranium dioxide have been widely investigated. The results of earlier investigations in this field have been reviewed by Lustman (1961).

The changes of the X-ray diffraction profiles of the 531 reflexions of natural UO_2 powders before and after exposure to a dose of $4 \, . \, 10^{18}$ fissions cm^{-3} at temperatures less than 100 °C have been studied by Boyko, Eichenberg, Roof & Halteman (1958). According to these results the line broadening after irradiation is due to the lattice strains. Berman, Bleiberg & Yenisavich (1960) have observed a slight lattice expansion after irradiation. It saturates at a fission density of less than $5 \, . \, 10^{16}$ fissions cm^{-3}. X-ray measurements of Waits (1972) have shown a logarithmic increase of the lattice parameter with dose up to about 10^{17} to 10^{18} fissions cm^{-3}. At still higher doses the lattice parameter decreases and remains constant in the range from 10^{18} to 10^{20} fissions cm^{-3}. The increase of the lattice parameter at 10^{16} fissions cm^{-3} is mainly due to the increasing concentration of interstitials clustered in loops, whereas the lattice-parameter decrease after still higher doses results from vacancy condensation.

These results are in agreement with electron microscopy studies of Whapham & Sheldon (1965) on fission damage in bulk uranium dioxide irradiated at ambient reactor temperature at doses yielding 10^{13} to $4{\cdot}3 \, . \, 10^{20}$ fissions cm^{-3}. At $4{\cdot}3 \, . \, 10^{15}$ fissions cm^{-3} clusters of about 25 Å diameter with the density of 10^{16} cm^{-3} are observed. With increasing dose these clusters grow into prismatic dislocation loops formed from interstitial atoms. The loops lie on {110} planes and have $\frac{1}{2}\langle 110 \rangle$ Burgers vectors. After irradiation with a dose corresponding to $6 \, . \, 10^{16}$ fissions cm^{-3} the average diameter of the loops is about 100 Å.

The objective of the present work has been the study of the influence of the lattice defects caused by neutron irradiation on the thermal diffuse scattering of X-rays. Specifically, our main interest has been focused on the question of whether scattering of X-rays by defect modes of lattice vibrations is observable.

Our work has been stimulated by the investigations of Tucker & Senio (1955) and Vance (1971). These authors have observed strong changes in the diffuse scattering by irradiating boron carbide (T & S) and diamond (V) with neutrons.

Experimental

The orientation of the crystals was carried out by taking back-reflexion photographs. The measurement of the diffuse-scattering intensity was also performed by evaluating back-reflexion patterns. The method applied was identical with the back-reflexion Laue technique except for using monochromatic Cu $K\alpha$ radiation. The monochromatization was accomplished by reflecting the copper radiation at a bent quartz crystal (Johannson technique).

Because of the high radioactivity of UO_2 after irradiation the specimens had to be made very small with a mass of approximately 10^{-4} g. Crystals with the shape of flat plates were cut with a diamond saw and polished with diamond powder. The final thickness of the specimens was about 0·03 mm. The flat surface of the plates deviated several degrees from the {111} plane. The samples were mounted with Tixo-tape on small plexiglas frames fastened to the goniometer head. The specimens were irradiated in the core of the ASTRA reactor at the Forschungszentrum Seibersdorf with doses of 10^{14}, 10^{15} and $5 \, . \, 10^{16}$ fissions cm^{-3}. Because of the very high radioactivity of ir-

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* On leave from the Institute for Nuclear Research, Swierk, Poland.

radiated uranium dioxide it has been impossible to study diffuse scattering in samples irradiated with doses higher than 5 . 10^{16} fissions cm^{-3}.

Since the primary X-ray beam was adjusted in such a way that it fell on the UO_2 single crystal along one of the main directions (⟨100⟩, ⟨110⟩ or ⟨111⟩) only a few reciprocal-lattice points lay close to the sphere of reflexion and gave diffuse scattered rays in the back directions. If the wave vector of the incident radiation $\mathbf{k}_0$ was parallel to the [111] direction, the reciprocal-lattice points 335, 353 and 533 had a distance of 0·045 Å^{-1} from the sphere of reflexion. A rotation of 8° of the crystal around the [$\bar{2}$20] direction brought the 335 reciprocal-lattice point exactly onto the sphere of reflexion.

Planes of high diffuse scattering in k space

Fig. 1 shows the diffuse scattering patterns of an UO_2 crystal with $\mathbf{k}_0$ positioned parallel to [111]. (*a*) represents the pattern before irradiation and (*b*) the photograph after irradiation with a dose of 5 . 10^{16} fissions cm^{-3}.

From these patterns one easily obtains the positions of the ends of the scattering vectors **k** in reciprocal space. The loci of these ends are diffuse circles lying on the sphere of reflexion. These diffuse circles correspond in the case of the unirradiated samples to some extent to the intersections of the $\{22\bar{4}\}_k$ and $\{11\bar{3}\}_k$ planes of the reciprocal lattice with the sphere of reflexion. For the irradiated specimens one has an approximate correspondence to the $\{002\}_k$ planes.

No observable changes in diffuse scattering could be registered after irradiation of UO_2 crystals with doses of 10^{14} and 10^{15} fissions cm^{-3}.

Constant-intensity contours

The diffuse-scattering pattern of the unirradiated sample [see Fig. 1(*a*)] exhibits a remarkable lowering of the diffuse-scattering intensity in areas in the neighbourhood of the corners of the white triangle. These areas correspond to the **q** vectors ($\mathbf{q}=\mathbf{k}-\mathbf{k}_0-\mathbf{g}$, **g**: reciprocal-lattice vector) nearly parallel to the [111] direction, a result which agrees with intensity calculations using the formula of Jahn (1942)

$$\begin{aligned}I \propto \frac{g^2}{q^2}\,\{&c_{44}^2+L^2[c_{44}(c_{11}-c_{44})\,(m^2+n^2)\\&+(c_{11}+c_{12})\,(c_{11}-c_{12}-2c_{44})m^2n^2]\\&+M^2[c_{44}(c_{11}-c_{44})\,(n^2+l^2)\\&+(c_{11}+c_{12})\,(c_{11}-c_{12}-2c_{44})n^2l^2]\\&+N^2[c_{44}(c_{11}-c_{44})\,(l^2+m^2)\\&+(c_{11}+c_{12})\,(c_{11}-c_{12}-2c_{44})l^2m^2]\\&-2MNmn(c_{12}+c_{44})\,[c_{44}+(c_{11}-c_{12}-2c_{44})l^2]\\&-2NLnl(c_{12}+c_{44})\,[c_{44}+(c_{11}-c_{12}-2c_{44})m^2]\\&-2LMlm(c_{12}+c_{44})\,[c_{44}+(c_{11}-c_{12}-2c_{44})n^2]\}\\&\div\{c_{11}c_{44}^2+c_{44}(c_{11}+c_{12})\,(c_{11}-c_{12}-2c_{44})\\&\times(l^2m^2+m^2n^2+n^2l^2)\\&\times(c_{11}+2c_{12}+c_{44})\,(c_{11}-c_{12}-2c_{44})^2l^2m^2n^2\}\end{aligned}$$

for the thermal diffuse intensity of cubic crystals. q and l,m,n are the length and the direction cosines of the **q** vector, g and L,M,N are the length and the direction cosines of the reciprocal-lattice vector, c_{11}, c_{12} and c_{44} are the elastic constants.

If one inserts into this formula the elastic constants

$$\begin{aligned}c_{11}&=40{\cdot}1\times10^{11}\,,\\c_{12}&=10{\cdot}8\times10^{11}\,,\\c_{44}&=6{\cdot}7\times10^{11}\ \text{dyn cm}^{-2},\end{aligned}$$

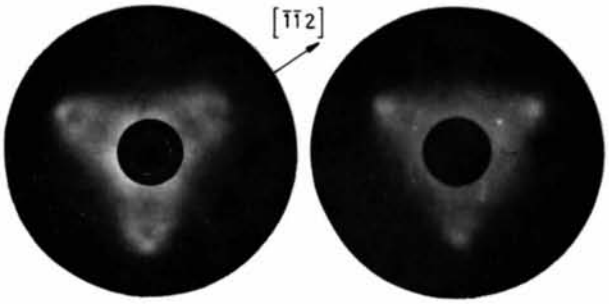
derived by Dolling, Cowley & Woods (1965) for UO_2, one obtains for the 335 reciprocal-lattice point the relative intensity values given in Table 1. The lowest values of intensity are obtained for [224] and [111]. The experimental data of Dolling *et al.* show that the frequency at a given distance from the reciprocal-lattice point is higher in the [111] direction than in the [001] direction. From this result one can conclude in agreement with the data of Table 1 that $I_{\text{diff.}[111]}$ has to be lower for a given distance from the lattice point than $I_{\text{diff.}[001]}$ since the diffuse scattering intensity varies at high temperatures with $(\text{frequency})^{-2}$.

Table 1. *Relative thermal diffuse scattering intensities in the vicinity of the* 335 *reciprocal-lattice point of* UO_2 *calculated from the Jahn formula*

Direction of **q** vector	*g/q* values 100	80	60	40	20
[$\bar{2}\bar{2}$4]	783	501	282	125	31·3
[002]	770	493	277	123	30·8
[224]	345	221	124	55·2	13·8
[111]	370	237	131	59·1	14·8
[331]	717	459	258	114	28·7
[220]	998	639	359	168	39·9
[33$\bar{1}$]	1032	660	371	165	41·3
[11$\bar{1}$]	830	531	299	133	33·3

The thermal diffuse intensity distribution in the neighbourhood of 335 for the constant length of the **q** vector of 0·012 Å^{-1} is plotted from the values given in Table 1 in Fig. 2(*a*). The isointensity contours are given in Fig. 2(*b*).

In order to determine experimentally the diffuse-scattering intensity distribution in the vicinity of the 335 point a series of photographs was taken of unirradiated and irradiated UO_2 samples. The crystal was turned in steps of 2° around the [$\bar{2}$20] axis after each exposure. In this way the $\mathbf{k}_0$ vector formed the angles −2, 0, 2, 4, 6, 8 and 10° with the [111] direction. At the 8° position the 335 lattice point lay exactly on the sphere of reflexion.



(*a*) (*b*)

Fig. 1. X-ray thermal diffuse pattern of a UO$_2$ single crystal with the wave vector $\mathbf{k}_0$ of the incident radiation parallel to the [111] direction. Cu $K\alpha$ radiation, 40 kV, 28 mA, 66 h, 40 mm crystal-to-film distance. Laue spots visible on photograph correspond to $\frac{1}{2}\lambda$ of Cu $K\alpha$. (*a*) Before irradiation, (*b*) After irradiation with a dose of $5 . 10^{16}$ fissions cm^{-3}.

The isointensity contours evaluated from measurements of the photographic density are shown in Fig. 3. A strong intensity maximum occurs in the [33$\bar{1}$] direction for unirradiated UO_2. For the irradiated UO_2 there is a weak [002] maximum visible.

Conclusion

The curves of Fig. 3 represent the combined effect of (1) the scattering on the normal and defect modes of the lattice vibrations and (2) the diffuse scattering on lattice defects introduced by the irradiation (Huang scattering in the neighbourhood of reciprocal-lattice points as well as Stokes–Wilson scattering for large $\mathbf{q}$ values). An experimental separation of the two types of scattering, which can be carried out only at low temperatures for which thermal diffuse scattering is negligible, has not yet been attempted.

Indications of the nature of the scattering process in the case of the irradiated sample can be deduced from the theoretical point of view. Since planar defect clusters (dislocation loops formed by interstitial atoms) of a radius of approximately 100 Å are produced at our dose of $5\cdot10^{16}$ fissions cm^{-3} (see *Introduction*) the Huang scattering region is limited to q values $<0\cdot01$ $Å^{-1}$. This region is indicated on Fig. 3(*b*). Since all our measurements lie outside this region one has to consider Stokes–Wilson scattering as a cause for the change in the diffuse scattering introduced by irradiation.

Stokes–Wilson scattering has been treated in a number of theoretical papers reviewed by Krivoglaz (1969) and Dederichs (1973). A decrease of the intensity proportional to $1/q^4$ or to $1/q^n$ with $n>4$ was calculated. This decrease predicted by the theory would be much faster than the one actually seen in our patterns. Analysis of the contours of Fig. 3(*b*) yields an average decrease slower than $1/q^3$. This fact would indicate that part of the observed diffuse intensity may be due to the scattering of X-rays by defect modes of lattice vibrations.

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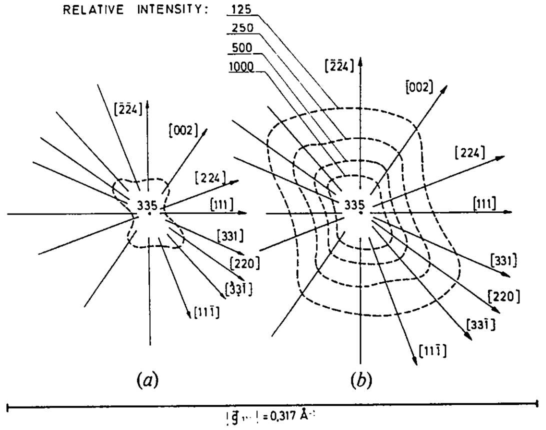

Fig. 2. Thermal-diffuse-intensity distribution in a UO_2 crystal around the 335 reciprocal-lattice point as calculated from the Jahn formula. (*a*) For $q=0\cdot012$ $Å^{-1}$ (*b*) Isointensity contours.

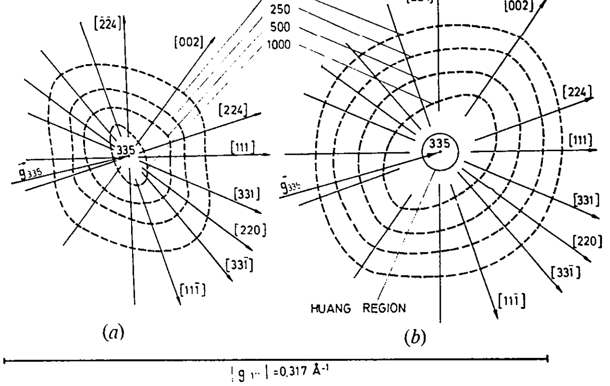

Fig. 3. Isointensity contours for a UO_2 crystal obtained from measurements of the density of the photographic films. (*a*) Unirradiated specimen. (*b*) Irradiated specimen ($5\,.\,10^{16}$ fissions cm^{-3}).

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