die Maxima der Absorptionsbanden von II in PVA und in PMAM, wie auch in verschiedenen Alkoholen fast dieselben Lagen haben. Dagegen sind die Fluoreszenzbandenmaxima von II in PVA und PMAM im Vergleich mit verschiedenen Alkoholen in Richtung kurzer Wellenlängen verschoben. Daraus kann man schließen, daß die zwischenmolekulare Wechselwirkung zwischen Lösungsmittel und gelösten Molekülen im angeregten Zustand größer ist als im Grundzustand [7, 8, 5].

Daß im Falle der hier untersuchten Verbindungen nur die β-Phosphoreszenz auftritt, kann durch die große Energiedifferenz zwischen dem normalen kurzlebigen Anregungszustand und dem metastabilen Zustand erklärt werden. Nach dem Jablonskischen [9, 10] Termschema ist die Energie zwischen dem normalen kurzlebigen Anregungszustand und dem metastabilen Zustand annähernd gleich $h\,c(\tilde{\nu}_F - \tilde{\nu}_P)$, wobei $\tilde{\nu}_F$ und $\tilde{\nu}_P$ die Wellenzahlen der Maxima von Fluoreszenz und β-Phosphoreszenz sind. Für I und II in PVA beträgt die Energiedifferenz dementsprechend etwa 0,63 eV bzw. 0,67 eV. Dagegen betrug für II in PMAM die Energiedifferenz 0,72 eV.

In Tab. 2 ist die mittlere Phosphoreszenzlebensdauer τ_P in sec und das Verhältnis der Phosphoreszenzintensität zur Fluoreszenzintensität I_P/I_F für I und II in PVA wiedergegeben. Der Einfluß der Methylgruppe bewirkt eine Verlängerung der mittleren Phosphoreszenzlebensdauer. Die mittleren Phosphoreszenzlebensdauern für II sind auch für die verschiedenen Lösungsmitteln PVA und PMAM deutlich verschieden.

Substanz	Erregungswellenlänge in mμ	Emissionswellenlänge in mμ	I_P/I_F bei 20 °C	τ_P (in sec) bei 20 °C
7-Oxycumarin	313	550	0,75	0,38
	366	550	0,42	—
4-Methyl-7-Oxycumarin	313	550	1,27	0,49
	366	550	0,58	—

Tab. 2.

[7] L. Bilot u. A. Kawski, Z. Naturforschg. **17 a**, 621 [1962].
[8] N. G. Bachschiew, Optika i Spektr. **10**, 717 [1961].
[9] A. Jablonski, Nature, Lond. **131**, 839 [1933].
[10] A. Jablonski, Z. Phys. **94**, 38 [1935].

Diffusion of Non-Gaseous Fission Products in UO_2 Single Crystals

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Although many data are available on the diffusion of gaseous fission products in UO_2, only few have so far been published on the diffusion of non-gaseous fission products. In the present work, an attempt was made to determine the diffusion constants of non-gaseous fission products, Ce, Ru, Zr-Nb, Sr, and Cs, in irradiated UO_2 single crystals, at temperatures ranging $1300-2500$ °C. UO_2 single crystals prepared by molten salt electrolysis, with the diameters of $0.4-1.0$ mm and apparently in octahedral or cubic shapes were used. They were irradiated in the JRR-2 (neutron flux, 2×10^{13} n/cm^2 sec) to 8.3×10^{17} fissions/cm^3 and were cooled for two months. In each experiment, a single crystal was placed or a UO_2 boat which was put inside a coiled tungsten filament subsequently heated for $10-30$ min with a current of $30-50$ A. in He atmosphere (Fig. 1). The temperature was calibrated by an optical pyrometer as well as by the melting point determination of pure metals.

γ-spectrum measurement of each sample before and after heating was performed to determine the released amounts of Ce, Ru and Zr-Nb and the fractional release was calculated from the difference of the peak heights. In cases of Sr, and Cs, radiochemical separations were performed and the specific activities of the two nuclides for the heated samples were compared with those for the unheated samples.

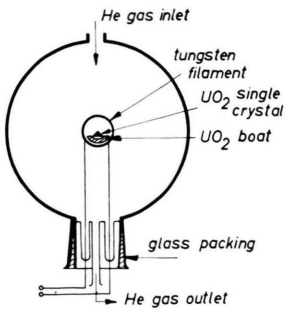

Fig. 1. Heating apparatus.

In contrast to the results of Shiriaeva and Tolmachev [1] who reported segregation of ^{99}Mo at the surface of UO_2 powder when heated to $400-1200$ °C, no segregation was observed in the present work for the fission products we examined. Therefore, we can assume that the diffusion of fission products was caused mainly by the release of them from the surface of single crystals. In

[1] L. V. Shiriaeva and Iu. M. Tolmachev, Atomnaya Energiya **3**, 318 [1957].

such a case, the diffusion constant D_i can be calculated according to the following equation, [2]

$$F_i = 2\sqrt{\frac{D_i t}{\pi}} \cdot \frac{S}{V} \quad \text{for } D_i t (S/V)^2 \ll 1$$

where F_i is the fraction of isotope i escaping a UO_2 single crystal with surface area S cm^2 and volume V cm^3 in t sec. In the actual calculation, S/V was evaluated from the weight of each sample by assuming a cube for the shape of each single crystal. In Fig. 2, the D_i's are plotted as functions of temperature T. The results are also summarized in the form

$$D_i = D_{0i} \exp(-Q_i/RT)$$

and are listed in Table 1.

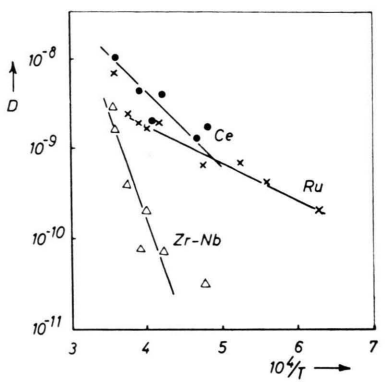

Fig. 2 a. Diffusion constants of Ce, Ru, and Zr—Nb in UO_2 single crystals.

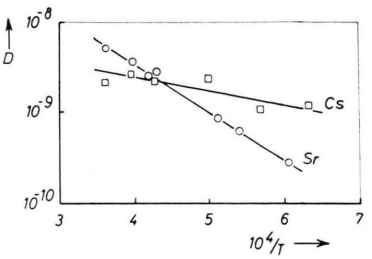

Fig. 2 b. Diffusion constants of Cs and Sr in UO_2 single crystals.

Of five nuclides examined, Zr-Nb has the highest activation energy, followed by Ce, while Cs has the lowest. The value D_{Zr} was determined by SCHMITZ and LINDNER [3] up to 1310 °C by using ^{95}Zr as a tracer. When the activation energies are compared, our data which were taken at much higher temperatures, seem to come out higher than those of SCHMITZ and LINDNER. It should however be taken into account that in our experiments, Zr is inclusive of its daughter nuclide Nb.

It is very difficult to compare the D values of non-gaseous and gaseous fission products because there is a very wide spread of D values in literatures for gaseous fission products [4]. However, non-gaseous fission products seem to have diffusion constants comparable with those of gaseous fission products.

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	D_i		D_i reported by SCHMITZ and LINDNER[3]*
Sr	$4.5 \times 10^{-7} \exp(-24{,}400/RT)$		
Zr-Nb	$1.67 \times 10^{-1} \exp(-104{,}000/RT)$	Zr	$1.6 \times 10^{-6} \exp(-59{,}200/RT)$
Ru	$8.61 \times 10^{-8} \exp(-19{,}200/RT)$		
Ce	$7.17 \times 10^{-6} \exp(-37{,}000/RT)$	Y	$6.8 \times 10^{-8} \exp(-46{,}400/RT$
Cs	$8.53 \times 10^{-9} \exp(-6{,}100/RT)$	Pm	$3.5 \times 10^{-6} \exp(-56{,}800/RT)$

* Determined at 1120 ~ 1450 °C by using sintered UO_2 pellets and radioactive tracers.

Table 1. Diffusion constants of non-gaseous fission products in UO_2: $D_i(\text{cm}^2/\text{sec}) = D_{0i}(\text{cm}^2/\text{sec}) \exp\{-Q_i(\text{cal/mol})/RT\}$.

[2] W. INTHOFF and K. E. ZIMEN, Trans. Chalmers Univ. Techn., No. 176 [1956].
[3] F. SCHMITZ and R. LINDNER, Z. Naturforschg. **16 a**, 1096 [1961].
[4] B. LUSTMAN, "UO_2: Properties and Nuclear Applications" (Ed., J. Belle) Chapter 9. U.S. Atomic Energy Commission, 1961.