[129]A. V. GROSSE, J. A. CAHILL and A. D. KIRSHENBAUM, *J. Am. Chem. Soc.* 83, 4665-4666 (1961).
[130]H. R. THRESH, D. W. G. WHITE, J. O. EDWARDS and J. W. MEIER, Dept. Mines and Tech. Surveys, Mines Branch, Phys. Met. Div., Ottawa, Canada, Report PM-R-61-19, Progress Report No. 1 (July 1961).
[131]E. GEBHARDT, M. BECKER and S. DORNER, *Z. Metallk* 45, 83-35 (1954).
[132]D. S. GATES and G. THODOS, *A. T. Ch. E. Journal* 6, 50-54 (1960).

S. W. Strauss*

Physical Metallurgy Branch,
Metallurgy Division
U. S. Naval Research Laboratory

Received June 19, 1963
Revised September 25, 1963

*Present Address
Headquarters, Research & Technology Division
Air Force Systems Command
RTD (RTHM) Physics Office
Balling Air Force Base
Washington, D.C. 20332

Considerations on the Mechanism of Inert-Gas Diffusion in UO₂

A large amount of work has been done in a number of laboratories in the U. S. A., in Canada and in Europe on the subject of inert-gas diffusion in solid nuclear fuels, and specially of xenon in UO_2,[1] this problem being of considerable importance in reactor design.

Information on inert-gas diffusion in some solids has been gained beforehand from the use of Hahn's emanation technique.[2] Moreover, experiments have been performed on the behavior of inert gases in metals,[3,4] and ionic crystals.[5,6] On the other side, a lot is known about some ion diffusion in UO_2.[7,8,9]

It turns out, therefore, that while experimental results of xenon diffusion-coefficient measurements in UO_2 are so widely scattered that, as Zimen pointed out recently,[6] one may feel justified in publishing almost any figures, some considerations on the migration mechanism are nevertheless possible. The scope of this short paper is merely to review in a critical way and, to a certain extent, to clarify and integrate current ideas on this subject, while suggesting at least one experiment that could cast a little more light on its intricacy.

The idea that inert gases can migrate in solids as charged ions instead of neutral atoms has been set forth by Tobin[4] for the following reasons:

1. When the gas is introduced into a metal through a glow discharge, the kinetic energy of the impinging atoms is of the order of 10 eV, corresponding to their ionization energy, whereas to displace an atom from the interior of the metal about 25 eV would be required:

2. a neutral inert-gas atom, being very large, would be a very serious misfit within a regular metal lattice;

3. the allegedly high strain energy associated with a neutral inert-gas atom within a metal lattice would result in its combination with the first few vacancies, which diffuse toward it;

4. the activation energies and, to a much lesser extent, the temperature-independent diffusion coefficients D_0 of Xe and Kr in Ag fit very well into the frame of a modified Lazarus theory if they are supposed to exist within the metal lattice as quasi-univalent positive ions.

That a neutral inert-gas atom would be such a misfit in any lattice may perhaps be questioned, since inert gases are highly compressible even in the solid state, as should be expected from the lack of strong Van der Waals interactions between atoms.

Stewart[10] has measured and Zucker[11] has calculated the compressibility of solid neon, argon and krypton. One sees that, even at very low temperature, the behavior is such that the compressibilities approach asymptotic temperature-independent values with increasing pressure. For argon the value is about 18×10^{-12} cm²/dyn, and for xenon, extrapolating from the other inert gases, about 14×10^{-12} cm²/dyn.

For UO_2, the Young modulus E should be, roughly extrapolating from Lang's data,[12] about (1.90 -

[1] For a comprehensive review and additional references, see: D. F. TONER and J. L. SCOTT, *Nucl. Safety*, 3, 15, (1961).
[2] See, for instance, F. FELIX and P. SCHMELING, *Euratom Report* EUR-111.e (1962).
[3] A. D. LeCLAIRE and A. H. ROWE, *Rev. Met.*, 52, 94 (1955).
[4] J. M. TOBIN, *Acta Met.*, 7, 701 (1959); 8, 781 (1960).
[5] T. LAGERWALL, *Nukleonik*, 4, 158 (1962).
[6] Oral communications of the Hahn-Meiter Institut Group at the Euratom Meeting on UO_2, Brussels (1962).
[7] A. B. AUSKERN and J. BELLE, *J. Nucl. Mat.*, 3, 267 (1961).
[8] J. BELLE and A. B. AUSKERN, *J. Nucl. Mat.*, 3, 311 (1961).
[9] H. M. FERRARI, Westinghouse Report WCAPD-2098 (1962).

[10] J. W. STEWART, *Phys. Rev.*, 97, 578 (1955).
[11] J. J. ZUCKER, *J. Chem. Phys.*, 25, 915 (1956); *Phil. Mag.*, 33, 937 (1958).
[12] See: J. BELLE and P. LUSTMAN, Westinghouse Report WAPD-184 (1957).

$0.00025\,T) \times 10^{12}$ dyn/cm^2, whence, if one assumes, like Childs,[13] the Poisson ratio to be about 0.17, in analogy with ThO$_2$, the compressibility is calculated to $(1.04 + 0.0002\,T) \times 10^{-12}$ cm^2/dyn, i.e., about one order of magnitude less than that for xenon at the high pressures supposed to exist in a solid lattice. The rather questionable assumption is made here that the xenon atom is nearly indefinitely compressible and the compressibility does not depend further on pressure. Then, if the xenon atom is substituted for a uranium ion or lies in the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ hole of the UO$_2$ fluorite structure, the equilibrium radius is[14]

$$R_0 = \frac{R + \alpha R'}{1 + \alpha},$$

R being the radius of the hole in the UO$_2$ matrix, $R' = 2.15$ Å, the radius of unstrained Xe atom and

$$\alpha = \frac{(1 + \nu)\chi}{2(1 - 2\nu)\chi'},$$

where χ and ν are the compressibility and the Poisson ratio of UO$_2$, and χ' the compressibility of Xe. Substituting the proper values at, say, $1800\,K$, one finds $R_0 = \sim 1.10\,A$.

Let us now turn to the strain energy W': in the xenon atom

$$\sigma = \rho = \text{const} = \frac{3}{\chi'}\,\ln\frac{R'}{R_0} = 1.43 \times 10^{11}\ \text{dyn/cm}^2,$$

whence

$$W' = \frac{\chi'}{2}\int_{v'}\sigma^2\,dv = \frac{\chi'}{2}\frac{4}{3}\pi R_0^3\sigma^2 = \sim 0.508\ \text{eV}.$$

In the UO$_2$ matrix, on the other hand,[15]

$$W = \frac{1}{2}\int_v (\sigma_r\,\epsilon_r + \sigma_\theta\,\epsilon_\theta)\,dv = 2\pi\frac{1 + 3\nu}{2E}\int_{R_0}^{\infty}\sigma^2 r^2\,dr =$$

$$= \pi\rho^2 R_0^6\frac{1 + 3\nu}{E}\int_{R_0}^{\infty}r^{-4}\,dr = \sim 0.045\ \text{eV}$$

so that the total strain energy would amount to ~ 0.553 eV.

It is hard to believe that the above computations give much more than a qualitative understanding of the whole matter: for instance, to take for χ' the value derived from measurements in the solid state means to neglect the Van der Waals interactions between the ions and the xenon atoms within the UO$_2$ matrix.

However, it is difficult to escape the following conclusions:

1. A xenon neutral atom is only slightly misfit in the UO$_2$ matrix, and hence
2. the strain energy to accommodate it is quite small.

These conclusions may likely be extended to other inert gases in solid lattices.

This does not rule out that inert gases might nevertheless migrate as ions, for the reasons set forth by Tobin.

Of course, experiments would be more convincing than theoretical devices: at the Hahn-Meitner Institut, in West Berlin, they have under way some on argon diffusion in irradiated alkali-doped CaF$_2$.[6]

Perhaps even stronger evidence can be gained from high-temperature solid-state electrolysis of neutron-irradiated KF (the neutron reactions of other halides are mostly unfavorable, and moreover Schottky disorder (which is typical of halides) allows both anionic and cationic conduction). Whether results for KF could be extended to halides with the fluorite structure and UO$_2$ is, of course, anybody's guess.

Ion diffusion in UO$_2$ has been measured for uranium, oxygen and nitrogen. In stoichiometric UO$_2$ uranium-ion diffusion is believed to be vacancy-controlled; the coefficient was measured to be 4.3×10^{-4} exp $(-88,000/RT)$cm^2/sec. Oxygen-ion diffusion was measured as $1.2 \times$ exp$(-65,300/RT)$ cm^2/sec. In non-stoichiometric UO$_2$ direct uranium-diffusion experiments were never performed, while for oxygen self-diffusion the best results, though somewhat uncertain, give an activation energy of 29,700 cal/mol, with D_0 depending on the O/U ratio (7.0×10^{-6} cm^2/sec for $O/U = 2.004$ and 2.06×10^{-3} cm^2/sec for $O/U = 2.063$).[7,8] If one agrees that uranium dioxide exhibits anti-Frenkel-type disorder and the oxygen-diffusion mechanism is the intersticialcy, then the energy to form a Frenkel pair in the oxygen sub-lattice is 71,200 cal/mol. The strong dependence of the elastic constants on the stoichiometry may account, at least in part, for the different values of D_0. Some indirect knowledge of the activation energy of the uranium ion diffusion in non-stoichiometric UO$_2$ can be derived from sintering experiments, which would indicate a figure in the range of 65,000 cal/mol.[16,17]

Nitrogen diffusion has been investigated by Ferrari,[9] who found an activation energy of 33,400 cal/mol. In this case (since, at high temperature,

[13] B. G. CHILDS, AECL Report CRMet-788 (1958).

[14] A. E. H. LOVE, Elasticity Cambridge, (1927); J. Friedel, Les dislocations Gauthier-Villars, (1956).

[15] See: A. M. FREUDENTHAL, in: C. F. Bonilla, *Nuclear Engineering* McGraw-Hill, (1957).

[16] R. L. COLOMBO, *Ric. Scient.*, in press: numerical data are in error, due to a miscalculation.

[17] I. AMATO, R. L. COLOMBO and A. M. PROTTI, *J. Nucl. Mat.*, in press.

UN in UO_2 is not stable in vacuum) a reasonable assumption is that nitrogen ions become free and occupy anionic and interstitial positions, whence they migrate through the intersticialcy mechanism, involving interchanges with the oxygen ions, the self-diffusion of which becomes the controlling factor. (Since nitrogen ions are somewhat bigger than oxygen ions, they are supposed to move faster, because they tend to make the lattice unstable[18]). Otherwise, the nitrogen ions might occupy only the interstitial positions $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $<\frac{1}{2}, 0, 0>$ and migrate jumping from one to a next neighbor in the $[1,1,0]$ directions.

Returning to xenon, one may remark that the Pauling univalent positive ion has the radius of 0.75 Å, while the univalent negative ion has the radius of 1.90 Å (comparable to that of a hypothetical di-valent nitrogen anion). Obviously, polyvalent ions would be smaller. It is very unfortunate that we cannot have any ideas of their compressibilities (except perhaps that they are, like any ions, very rigid), because of the inexistence of ionic xenon compounds.

However, one may attempt to draw the following conclusions:

—if xenon is in the neutral atomic state, then probably it occupies interstitial sites and moves by jumping directly from one to another, its diffusion energy being in this case of the order of 30,000 cal/mol;

—if xenon is a positive ion, it occupies cationic sites, whence it diffuses like a uranium ion, being smaller and having a somewhat lower activation energy (though higher than the energy of formation of a cation vacancy);

—if xenon is a negative ion, either it occupies interstitial sites or both anionic and interstitial sites, moving in one of the ways proposed previously for nitrogen, with activation energies in the range of 30,000 cal/mol.

Diffusion experiments carried out up to date do not allow conclusions. The B.M.I. Group[19] found 30,200 cal/mol for xenon diffusion from a fused UO_2 single crystal; though the experiment was very accurate, fused UO_2 always contains carbides, nitrides and other impurities, which make its use questionable. Almost all of the other researchers measured higher energies (sometimes in excess of 100,000 cal/mol) using UO_2 powders and polycrystalline sinters; if one is tempted to reject their results, because too many factors (including surface conditions, grain boundaries and inhomogeneities) might have interfered, he must very well consider also that the experiments on urani-

um, oxygen and nitrogen diffusion have been carried out on these "undesirable" materials.

Activation energies for krypton diffusion in UO_2 have been measured more seldom than for xenon, but the results lie well in the same range established for the latter.

This paper ends with a remark. In xenon and krypton diffusion experiments with UO_2 and UC, it has always been found that a sudden gas release (burst), much larger than would be expected from the solution of the diffusion equations for the transient period, takes place any time the temperature is stabilized at a certain level. Similar features are reported by Kelly[20] for the release of argon and xenon radiatively absorbed on Nb_2O_5, SiO_2 and TiO_2, by the Hahn-Meiter Institut Group for argon diffusion from fluorides,[6] by Bauer for xenon diffusion from stainless steel[21] and by Ferrari for nitrogen diffusion from UO_2.[9]

Thus, the so-called "burst-effect" is turning out to be not typical of any particular kind of solids (having been reported for ionic and covalent compounds and metals as well), nor of inert gases alone (since nitrogen is not), nor of any way of introducing the gas into the solid (fission, neutron capture, knocking-in, chemical decomposition and fission-product bombardment having been used).

The only common feature to all cases is the little chemical affinity, at the experimental conditions, of the diffusing gas to the lattice atoms; one may be left with the impression that the "burst-effect" is a much more general phenomenon in gas diffusion through solids than supposed.

R. L. Colombo

Fiat, Sezione Energia Nucleare, Torino

[18] A. FERRO, J. Appl. Phys., 28, 895 (1958).
[19] R. H. BARNES et al., Battelle Memorial Institute Report BMI-1533 (1961).

[20] R. KELLY, Can. J. Chem., 39, 2411 (1961).
[21] J. BUGL, oral communication at the Euratom Meeting on UO_2, Brussels (1962).

Measurement of Doppler Coefficient by Heating a Small Region of a Fast Reactor Critical Assembly*

Several of the methods proposed for measuring the Doppler coefficient in a fast critical facility involve heating only a very small region of the reactor. (The oscillating-rod Doppler experiment is one example.) It has been recognized that there is a difficulty in interpreting the results of such