

Diffusion in Gamma Uranium*

N. L. PETERSON AND S. J. ROTHMAN

Argonne National Laboratory, Argonne, Illinois

The diffusion of radioactive Cr, Mn, Fe, Co, Ni, Cu, and Nb tracers in bcc gamma uranium has been measured from 780 to 1080°C, using the thin-layer sectioning technique. The Arrhenius plots are curved at low temperatures; the curvature is not due to diffusion along grain boundaries or dislocations, or to defects introduced by the β - γ phase transformation. The activation energies and frequency factors calculated from the linear portion of the Arrhenius plots above the bend are very low (12–39 kcal/mol, 10^{-4} – 10^{-2} cm²/sec) and do not agree quantitatively with any known theory of impurity diffusion. The motion of Kirkendall markers in a very small chemical concentration gradient indicates that diffusion is by a defect mechanism; considerations of atomic size rule out interstitials as the defects. Co and Fe diffuse very fast ($D \approx 2 \times 10^{-6}$ cm²/sec at 950°C), indicating a strong Co- (or Fe-) vacancy binding energy, and a high degree of correlation between the directions of successive vacancy jumps. This is substantiated by the acceleration of self-diffusion in γ -U by addition of Co.

INTRODUCTION

A GREAT deal is now known about diffusion in fcc metals.¹ The important points are: (1) Diffusion takes place by the vacancy mechanism.² (2) The temperature dependence of the diffusion coefficient D fits an Arrhenius-type relation¹:

$$D = D_0 e^{-Q/RT}. \quad (1)$$

(3) The activation energy for self-diffusion is related to the absolute melting temperature by³

$$Q(\text{in cal/mol}) = 35T_m (\text{in } ^\circ\text{K}). \quad (2)$$

(4) The entropy of activation for self-diffusion is positive (Zener's rule⁴), giving $D_0 \geq 0.1$ cm²/sec. (5) The difference between the activation energies for impurity and self-diffusion in a noble metal depends on the excess valence of the impurity, and can be calculated from the electrostatic interaction between the vacancy and the impurity, using the Fermi-Thomas equation.⁵

Points (2)–(4) also describe diffusion in bcc alkali metals^{6,7} and in the bcc transition metals Nb,^{8,9} Mo,¹⁰ and W.¹¹ Diffusion in the bcc phases of the metals Ti, Zr, and U is different. The Arrhenius plots for diffusion

in Ti,^{12,13} and Zr¹⁴ are curved. Whether the Arrhenius plot for self-diffusion in γ -U is also curved is not clear because the data are somewhat scattered,^{15–17} but Q and D_0 for self-diffusion in γ -U are certainly much lower, 26.7 kcal/mol and 1.2×10^{-3} cm²/sec, respectively, than predicted from rules 3 and 4 above.

A number of chemical diffusion studies on γ -U systems^{18,19} showed a strong Kirkendall effect,²⁰ which indicates that diffusion takes place by a defect mechanism. There has been only one tracer measurement of impurity diffusion in γ -U,²¹ so it seemed worthwhile to make a systematic study of tracer diffusion in γ -U with the hope that a regular variation of Q and D_0 with the valence or atomic size of the solute atoms might somehow help us to understand the "anomalous" self-diffusion in this material. These studies in turn suggested some additional experiments: the measurement of marker movement (Kirkendall effect) during diffusion in a very small concentration gradient, the presence of which indicates that diffusion is by a defect mechanism, the measurement of the effect of small impurity additions on self-diffusion, and a study of the effect of the β - γ phase transformation on diffusion in γ -U.

* This work was performed under the auspices of the U. S. Atomic Energy Commission.

¹ D. Lazarus, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 71.

² N. L. Peterson, *Phys. Rev.* **136**, A568 (1964).

³ G. V. Kidson and R. Ross, in *Radioisotopes in Scientific Research* (Pergamon Press, Inc., New York, 1958), p. 185.

⁴ C. Zener, *J. Appl. Phys.* **22**, 372 (1951).

⁵ A. D. LeClaire, *Phil. Mag.* **7**, 141 (1962).

⁶ N. H. Nachtrieb, E. Catalano, and J. A. Weil, *J. Chem. Phys.* **20**, 1185 (1952).

⁷ A. N. Naumov and G. Y. Riskin, *Zh. Tekhn. Fiz.* **29**, 189 (1959).

⁸ R. Resnick and L. S. Castleman, *Trans. AIME* **218**, 307 (1960).

⁹ R. F. Peart, D. Graham, and D. H. Tomlin, *Acta Met.* **10**, 519 (1962).

¹⁰ J. Askill and D. H. Tomlin, *Phil. Mag.* **8**, 997 (1963).

¹¹ R. L. Andelin, Los Alamos Scientific Laboratory Report LA-2880, 1963 (unpublished).

¹² R. F. Peart and D. H. Tomlin, *Acta Met.* **10**, 123 (1962).

¹³ G. B. Gibbs, D. Graham, and D. H. Tomlin, *Phil. Mag.* **8**, 1269 (1963).

¹⁴ J. I. Federer and T. S. Lundy, *Trans. AIME* **227**, 592 (1963).

¹⁵ A. Bochvar, V. Kuznetsova, and V. Sergeev, in *Transactions of the Second Geneva Conference on the Peaceful Uses of Atomic Energy* (United Nations, Geneva, 1958), Vol. VI, p. 68.

¹⁶ Y. Adda and A. Kirianenko, *J. Nucl. Mater.* **1**, 120 (1959).

¹⁷ S. J. Rothman, L. T. Lloyd, and A. L. Harkness, *Trans. AIME* **218**, 605 (1960).

¹⁸ Y. Adda and J. Philibert, in *Transactions of the Second Geneva Conference on the Peaceful Uses of Atomic Energy* (United Nations, Geneva, 1958), paper 1160, 1958, *Compt. Rend.* **242**, 3081 (1956); **243**, 1115 (1956); **246**, 113 (1958); **249**, 2775 (1960); *Rev. Metal. (Paris)* **54**, 597 (1957); **57**, 549 (1960); *Acta Met.* **8**, 700 (1960).

¹⁹ N. L. Peterson and R. E. Ogilvie, *Trans. AIME* **227**, 1083 (1963).

²⁰ A. D. Smigelskas and E. O. Kirkendall, *Trans. AIME* **171**, 130 (1947).

²¹ S. J. Rothman, *J. Nucl. Mat.* **3**, 77 (1961).

EXPERIMENTAL

Specimen Preparation

The basis metal used in the tracer diffusion experiments was uranium containing less than 100 ppm by weight of total impurities. The ingots were rolled, swaged, and turned to 1 cm diam. Pieces about 0.7 cm long were cut off, water quenched from 720°C and annealed at 450°C. This heat treatment was intended to give small, randomly oriented α grains and thus decrease surface roughening during heating. The end face on which the isotope was to be deposited was ground and polished through 1- μ diamond paste and electropolished. The isotopes used, their method of production and deposition, and the radiation counted are given in Table I. The thickness of the isotope layers was in all cases $\ll (Di)^{1/2}$.

The alloys for the study of the effect of Co on self-diffusion in γ -U were made from depleted (0.033% U²³⁵), high-purity U, and radioactive Co (see Table II). The specific activity of Co⁶⁰ from the sections varied no more than 3% in a sample, indicating that the alloys were homogenous. A thin layer of the diffusing isotope U²³⁵ was deposited by sputtering.²² For the Kirkendall-effect study, a piece of high-purity U alloyed with 0.407 at.% Co was pressed together with a piece of pure U in a Ta picture frame, with Ta-foil and W-wire markers.

TABLE I. Radio isotopes used in this study.

Isotope	Method of production	Method of deposition	Radiation counted
Cr ⁵¹	Neutron irradiation of Cr metal	Evaporation ^a	0.320-MeV photopeak
Mn ⁵⁴	Neutron irradiation of natural Fe (<i>n,p</i>) reaction on Fe ⁵⁴	Evaporation of iron	0.84-MeV ^b photopeak
Fe ⁵⁹	Obtained from ORNL	Electroplated on 2.5 μ Fe foil, evaporation of foil	1.098 and 1.298 MeV photopeaks
Co ⁶⁰	Neutron irradiation of Co metal	Evaporation	1.17- and 1.33-MeV photopeaks
Ni ⁶³	Obtained from ORNL	Electroplated on 2.5 μ Ni foil, evaporation of foil	Beta counted (see text)
Cu ⁶⁴	Neutron irradiation of Cu metal	Evaporation	0.511-MeV annihilation radiation
Nb ⁹⁵	Obtained from ORNL	Oxalate solution dropped on sample surface and dried ^c	0.745-MeV photopeak

^a See Ref. 21 for a description of the evaporation equipment and techniques.

^b The Compton-scattered radiation from Fe⁵⁹ was subtracted out.

^c The sample surface was ground on No. 600 grit paper directly before deposition of the isotope.

²² R. Weil, S. J. Rothman, and L. T. Lloyd, *Rev. Sci. Instr.* **30**, 541 (1959).

TABLE II. Influence of Co on self-diffusion in γ -U.

at.% Co	Annealing temp. (°C)	Annealing time (10 ³ sec)	D (10 ⁻⁹ cm ² /sec)
0.457	822.4	31.86	10.6
0.227	822.4	31.86	6.53
0.420	939.7	10.44	28.5
0.254	939.7	10.44	22.5

Annealing

Two samples with the same isotope deposited on them were placed with their radioactive faces together into a Ta cup, which, together with some Zr getter, was sealed off in a quartz tube under a vacuum of 2×10^{-5} Torr. The samples were annealed in resistance heated furnaces and the annealing temperature was measured by a Pt/Pt-10% Rh thermocouple in the heat sink.²³ The diffusion time was corrected for heating up to the diffusion temperature. The Kirkendall sample was annealed in the picture frame in a dynamic vacuum of 2×10^{-6} Torr. Chemical analysis of a tracer diffusion sample after the diffusion anneal showed no significant impurity pickup during the anneal.

To investigate the possible effect of imperfections generated by the β - γ phase transformation on diffusion in γ -U, the following experiment was done²⁴: A piece of high-purity U, prepared as above, and with a thermocouple in one end, was annealed in a dynamic vacuum of 2×10^{-6} Torr at 1098°C for 19.5 h. Its temperature was then lowered to 809.7°C without going into the β phase, a layer of Co⁶⁰ was evaporated on to the other end, and the sample was diffused for $\frac{1}{2}$ h.

Sectioning and Counting

The samples were sectioned on a precision lathe as described before.^{17,23} Ten to twelve sections, 0.005–0.030-cm thick, were taken from each sample; the section thicknesses were determined from the chip weights and were corrected to their values at the temperature of the diffusion anneal using the thermal expansion data of Chiotti *et al.*²⁵ Weight losses were $\leq 1\%$. The sections were counted as chips in the beakers in which they were caught, except for the Mn runs and some of the Cr runs, where the sections were dissolved and an aliquot taken for counting. A 7.5-cm \times 7.5-cm NaI-Tl scintillation crystal with a single-channel analyzer and scaler was used. The first section was counted before and after each succeeding section and used to correct for analyzer drift and radioactive decay. Corrections were made for background and the activity due to the uranium. More than 10 000 counts above

²³ N. L. Peterson, *Phys. Rev.* **132**, 2471 (1963).

²⁴ W. C. Hagel, *Trans. AIME* **227**, 267 (1963).

²⁵ P. Chiotti, H. H. Klepfer, and R. W. White, *Trans. ASM* **51**, 772 (1959).

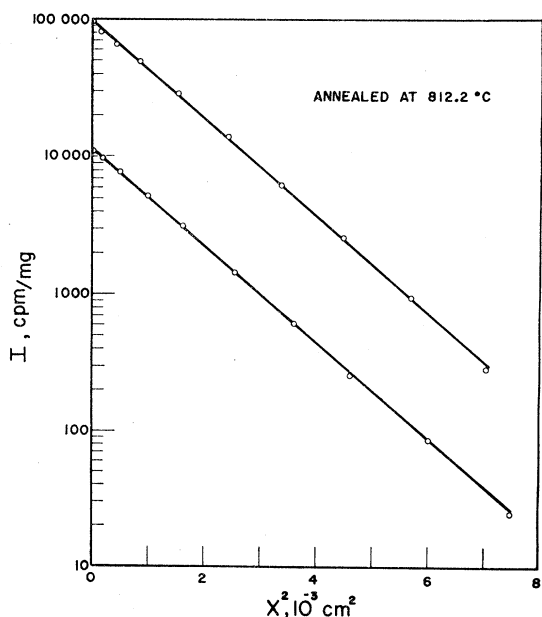


FIG. 1. Penetration plots for the diffusion of Cu in γ -U. The two samples were annealed simultaneously. The plots are separated along the ordinate by one decade for clarity.

background were taken from all sections except for the Mn isotope.

Since the β radiation from Ni^{63} is too weak to be counted as above, the Ni^{63} was separated chemically from the dissolved sections by extracting it into a toluene-base scintillating solution, and counted therein.²⁶ The U^{235} concentrations in the self-diffusion runs were determined by fission counting.^{27,28} The raw data and a fuller description of the experimental details are given in Ref. 29.

RESULTS

The solution of the diffusion equation for the initial and boundary conditions of the tracer-diffusion experiments is³⁰

$$I = \frac{M}{(\pi Dt)^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right), \quad (3)$$

where I is the concentration or specific activity of the diffusing isotope in a section, x is the distance of the center of the section from the original surface, M is the quantity of isotope deposited originally, t the annealing time, and D the diffusion coefficient. The plots of $\log I$ versus x^2 (penetration plots) (Fig. 1) were linear,

²⁶ The chemistry and counting were done by J. J. Hines and M. Essling.

²⁷ J. Gray, Jr. and F. Hagemann, *Rev. Sci. Instr.* **33**, 1258 (1962).

²⁸ S. J. Rothman, J. Gray, Jr., J. P. Hughes, and A. L. Harkness, *J. Nucl. Mat.* **3**, 72 (1961).

²⁹ N. L. Peterson and S. J. Rothman, Argonne National Laboratory Report ANL-6568, 1964 (in preparation).

³⁰ J. Crank, *The Mathematics of Diffusion* (Oxford University Press, London, 1957), p. 11.

even at the lowest annealing temperatures, indicating that the initial and boundary conditions were fulfilled, and that there was no grain-boundary diffusion. Values of D obtained by least-squares analyses of these data are given together with the annealing temperatures and times in Table III, and are plotted versus $1/T$ in Fig. 2. The errors in D due to sectioning and counting are estimated to be 3% for the diffusion of all impurities except Mn, 10% for the diffusion of Mn, and 7% for the self-diffusion runs, plus 1 to 2% error due to a $\pm 1^\circ\text{C}$ uncertainty in the temperature. It should be noted that D_{Co} in the specially pre-annealed sample (see text, asterisk in Fig. 2) agrees with results from conventionally annealed samples within the experimental error.

The effect of Co on self-diffusion in γ -U is shown in Fig. 3 and Table II, and the marker movement in the Kirkendall effect experiment, 12μ in 18.4 h at 915°C , is shown in Fig. 4.

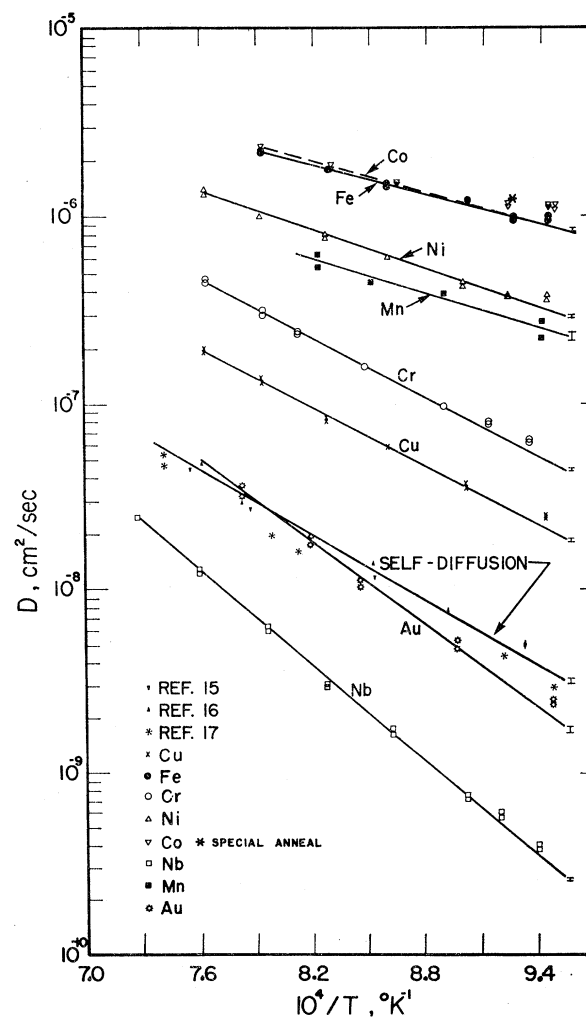


FIG. 2. Arrhenius plots for diffusion in γ -U. The limits of error in D are indicated by I.

TABLE III. Tracer diffusion in γ -U.

Element	Annealing time (10 ³ sec)	Temp. (°C)	<i>D</i> (cm ² /sec)	Element	Annealing time (10 ³ sec)	Temp. (°C)	<i>D</i> (cm ² /sec)		
Co	2.67	783.3	1.09×10 ⁻⁶	Ni	2.66	786.9	3.68×10 ⁻⁷		
	2.67	783.3	1.14×10 ⁻⁶		2.66	786.9	3.64×10 ⁻⁷		
	6.27	786.1	1.13×10 ⁻⁶		3.01	811.5	3.81×10 ⁻⁷		
	6.27	786.1	1.15×10 ⁻⁶		3.01	811.5	3.77×10 ⁻⁷		
	3.20	811.5	1.16×10 ⁻⁶		3.08	839.1	4.51×10 ⁻⁷		
	3.20	811.5	1.20×10 ⁻⁶		3.08	839.1	4.39×10 ⁻⁷		
	3.08	837.4	1.17×10 ⁻⁶		3.17	891.9	6.20×10 ⁻⁷		
	3.08	837.4	1.19×10 ⁻⁶		3.17	891.9	6.19×10 ⁻⁷		
	3.17	885.5	1.49×10 ⁻⁶		3.24	937.3	7.73×10 ⁻⁷		
	3.17	885.5	1.52×10 ⁻⁶		3.24	937.3	7.99×10 ⁻⁷		
	3.24	937.3	1.87×10 ⁻⁶		3.31	990.9	9.96×10 ⁻⁷		
	3.24	937.3	1.78×10 ⁻⁶		3.31	990.9	9.99×10 ⁻⁷		
	3.31	989.2	2.31×10 ⁻⁶		3.33	1039.2	1.34×10 ⁻⁶		
	3.31	989.2	2.45×10 ⁻⁶		3.33	1039.2	1.42×10 ⁻⁶		
	1.84	809.7	1.20×10 ^{-6a}						
	Mn	5.40	787.0		2.29×10 ⁻⁷	Cu	13.47	786.6	2.50×10 ⁻⁸
		5.40	787.0		2.78×10 ⁻⁷		13.47	786.6	2.44×10 ⁻⁸
7.02		847.1	3.90×10 ⁻⁷	10.21	812.2		3.01×10 ⁻⁸		
7.02		898.5	4.46×10 ⁻⁷	10.21	812.2		2.98×10 ⁻⁸		
1.74		938.8	6.33×10 ⁻⁷	10.28	838.1		3.78×10 ⁻⁸		
1.74		938.8	5.43×10 ⁻⁷	10.28	838.1		3.63×10 ⁻⁸		
				10.37	891.2		5.88×10 ⁻⁸		
Fe	2.67	786.9	9.50×10 ⁻⁷	10.37	891.2		5.93×10 ⁻⁸		
	2.67	786.9	9.80×10 ⁻⁷	10.44	935.6		8.53×10 ⁻⁸		
	3.01	808.5	9.66×10 ⁻⁷	10.44	935.6		8.22×10 ⁻⁸		
	3.01	808.5	9.97×10 ⁻⁷	10.51	989.8		1.31×10 ⁻⁷		
	3.08	836.9	1.17×10 ⁻⁶	10.51	989.8		1.38×10 ⁻⁷		
	3.08	836.9	1.22×10 ⁻⁶	9.93	1039.2		1.97×10 ⁻⁷		
	3.17	892.7	1.50×10 ⁻⁶	9.93	1039.2		1.94×10 ⁻⁷		
	3.17	892.7	1.47×10 ⁻⁶						
	3.24	934.7	1.80×10 ⁻⁶	Nb	432.90	790.7	3.87×10 ⁻¹⁰		
	3.24	934.7	1.80×10 ⁻⁶		432.90	790.7	3.97×10 ⁻¹⁰		
	3.49	989.6	2.21×10 ⁻⁶		240.80	813.9	5.93×10 ⁻¹⁰		
	3.49	989.6	2.26×10 ⁻⁶		240.80	813.9	6.24×10 ⁻¹⁰		
			179.30		835.5	7.30×10 ⁻¹⁰			
Cr	10.80	797.4	6.33×10 ⁻⁸		179.30	835.5	7.65×10 ⁻¹⁰		
	10.80	797.4	6.48×10 ⁻⁸		78.77	887.2	1.80×10 ⁻⁹		
	10.22	822.9	7.90×10 ⁻⁸		78.77	887.2	1.68×10 ⁻⁹		
	10.22	822.9	8.03×10 ⁻⁸		54.72	936.0	3.08×10 ⁻⁹		
	23.40	851.1	9.82×10 ⁻⁸		54.72	936.0	2.99×10 ⁻⁹		
	13.20	908.3	1.61×10 ⁻⁷	19.51	983.5	6.36×10 ⁻⁹			
	3.60	957.6	2.45×10 ⁻⁷	19.51	983.5	6.16×10 ⁻⁹			
	3.60	957.6	2.43×10 ⁻⁷	19.53	1044.9	1.25×10 ⁻⁸			
	3.31	987.5	3.01×10 ⁻⁷	19.53	1044.9	1.29×10 ⁻⁸			
	3.31	987.5	3.19×10 ⁻⁷	14.33	1102.2	2.52×10 ⁻⁸			
	3.09	1037.4	4.67×10 ⁻⁷	14.33	1102.2	2.50×10 ⁻⁸			
	3.09	1037.4	4.58×10 ⁻⁷						

* Preannealed at 1098°C for 19½ h.

DISCUSSION

Curved Arrhenius Plots

The most striking feature of these results is the curvature of the plots of $\log D$ versus $1/T$ for the diffusion of Co, Fe, Cr, Ni, and Cu in γ -U (Fig. 2). Although the scatter in the data does not allow us to say whether the plots are curved along their entire length, or whether the high-temperature part is straight, the curvature at about 830°C is very definitely greater than the experimental error. For example, for Co the points at 783.3°C lie about 25% above the line drawn through the high-temperature points, while the total error in D is about 3.5%. Such behavior is found neither in fcc metals¹ (except for some slight dislocation

effects^{31,32}), nor in a number of bcc transition metals (Nb,^{8,9} Mo,¹⁰ W¹¹), and is very similar to the "anomalous diffusion" found in bcc Zr (Ref. 14) and Ti (Ref. 13). These curved plots differ from the Arrhenius plot for self-diffusion in γ -U,¹⁵⁻¹⁷ which is either not curved, or curved far less than the plots for the diffusion of Co, Fe, Cr, Ni, and Cu (Fig. 2).

Curved Arrhenius plots are usually considered to be caused by (1) experimental error; (2) a grain-boundary diffusion component; (3) diffusion along dislocations; (4) nonequilibrium defects introduced by a phase transformation³³; or (5) excess defects introduced by

³¹ E. W. Hart, Acta Met. 5, 597 (1957).

³² C. T. Tomizuka, Acta Met. 6, 660 (1958).

³³ P. L. Gruzin, E. V. Kuznetsov, and G. V. Kurdyumov, in

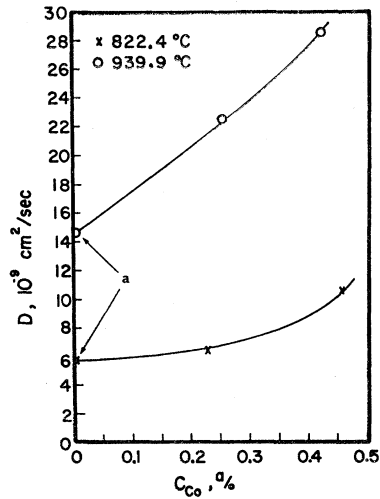


FIG. 3. The effect of Co on self-diffusion in γ -U: plot of D (self) versus Co concentration. Points (a) from Ref. 17.

residual impurities.³⁴ We consider that the first four are very unlikely for the following reasons:

(1) The reproducibility of our data, e.g. the two Co diffusion runs at 783.3 and 786.1 °C, the quality of the penetration plots, and a detailed analysis of the errors²⁹ indicate that experimental errors are far too small to produce these deviations from linearity.

(2) The linearity of the $\log I$ versus x^2 plots (Fig. 1), plus the large grain size of γ -U (0.2–5 mm¹⁷) indicate that grain-boundary diffusion can be neglected.

(3) Diffusion along dislocations seems possible, but not too likely. Using Mortlock's³⁵ formula and assuming that the Co concentration at dislocations is 100 times the Co concentration in the lattice away from dislocations and that the diffusion coefficient in the dislocation pipes is 10^{-4} cm²/sec, we calculate that a minimum of 2.5×10^9 dislocations/cm² are necessary to cause the observed low-temperature enhancement of

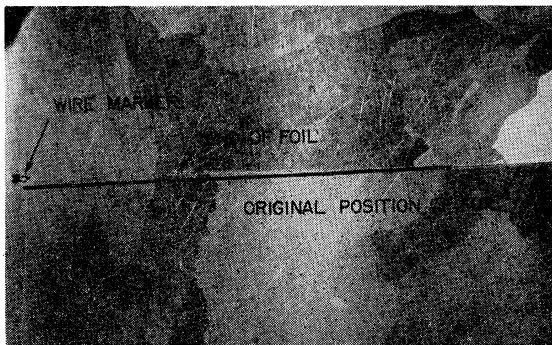


FIG. 4. Kirkendall marker movement during interdiffusion of pure U (bottom) and a U-0.407 at.% Co alloy (top). (Polarized light illumination, 82 \times .)

Problems of Metallography and the Physics of Metals, edited by B. Y. Lyubov (Metallurgizdat, Moscow, 1955) [English transl.: AEC-tr-2924, p. 343].

³⁴ G. V. Kidson, *Can. J. Phys.* **41**, 1563 (1963).

³⁵ A. J. Mortlock, *Acta Met.* **8**, 132 (1960).

the diffusion of Co. We think that the density of dislocations in γ -U is much lower, since the large grain size of γ -U indicates that recrystallization and grain growth have taken place, and the density of dislocation in a recrystallized metal is 3 orders of magnitude lower, e.g. 6×10^5 in Nb.³⁶ In the preannealed sample, further elimination of dislocations due to climb, as observed by Young and Cabrera³⁷ on Cu annealed at 1000 °C, probably took place and yet the preanneal did not change the value of D . It is therefore safe to say that if dislocations in γ -U behave as dislocations in other metals do, their influence on diffusion in γ -U is small.

(4) The results on the preannealed sample also show that mechanism (4) is not operative in γ -U, since almost any nonequilibrium defect should have been annealed out.

Kidson's hypothesis,³⁴ that excess vacancies are introduced by the strains around interstitial impurities, can explain the present data. We are not convinced that this is really the reason for the curved Arrhenius plots because if there were an extrinsic region and an intrinsic region, the Arrhenius plot for self-diffusion should be curved much more than it is. Point defects introduced by impurities should produce more curvature in the Arrhenius plots for large Q than for small Q , which is the opposite of what is observed. It is also unlikely that the vacancies are introduced by the diffusing isotope; varying the Co concentration by a large factor did not change D_{Co} .

Nevertheless, following Kidson³⁴ and Gibbs *et al.*,¹³ we have attempted to fit our data to the sum of two exponentials,

$$D = D_{01}e^{-Q_1/RT} + D_{02}e^{-Q_2/RT}, \quad (4)$$

where the subscripts 1 and 2 refer to the intrinsic and extrinsic regions, respectively. The fitting, done by a least-squares method,³⁸ produced some odd results. It seems that because of the relatively small change of D in a narrow temperature range, the value of Q_1 can be changed by a factor of more than 2 without appreciably changing the accuracy of the fit of Eq. (4) to the data. Thus, we cannot attach much importance to these Q_1 's and D_{01} 's, even though they can be made "reasonable," i.e., they can be made to agree with the melting point rule and Zener's theory. The interesting value that comes out of these calculations is D_{02} , which is in all cases of the order of 10^{-6} cm²/sec, indicating that mechanism No. 2 probably involves a temperature independent defect concentration, or it is some unspecified mechanism with a very large negative entropy of activation.

It appears then that none of the commonly given explanations for curved Arrhenius plots can definitely

³⁶ T. J. Koppelaar and P. R. V. Evans, *J. Inst. Metals* **92**, 238 (1964).

³⁷ F. W. Young, Jr. and N. Cabrera, *J. Appl. Phys.* **28**, 787 (1957).

³⁸ B. Garbow (private communication).

be chosen as the true one for γ -U. Grain boundaries and defects introduced by the phase transformation are out, and dislocations are improbable. Residual impurities may play an important role, although we do not consider this mechanism to be definitely established.

The Mechanism of Diffusion

The presence of a Kirkendall effect in both the U-U +0.407 at.% Co couple (Fig. 4) and in U-U+10 at.% Nb couples¹⁹ shows that diffusion in these two systems takes place by a defect mechanism. Since the value of D changes gradually between D_{Nb} and D_{Co} (Fig. 2), it appears safe to assume that all these tracers, as well as U and Au, diffuse by the same defect mechanism.

The defects involved in diffusion are usually considered to be either vacancies or interstitials. We consider that interstitials are unlikely because the tracer atoms are large relative to the holes in the γ -U lattice; the Goldschmidt radii of the tracers range from 1.244 Å (Ni) to 1.456 Å (Nb),³⁹ and the largest sphere that can be put into the interstices of the γ -U lattice is 0.424 Å radius.⁴⁰ We emphasize that interstitials are not eliminated by these arguments as conclusively as they would be by a Balluffi-Simmons⁴¹ or isotope effect experiment.²

The Activation Energies for Impurity Diffusion

If the slopes of the high-temperature, straight-line parts of the $\log D$ versus $1/T$ plots (Table IV) are true activation energies, it becomes worthwhile to compare them with some of the current theories of impurity diffusion in metals. These comparisons are difficult to make quantitatively, because the theories require knowledge of the electronic structure, elastic constants, etc. of γ -U, and these are not well-known. Therefore, only qualitative agreement can be expected, and so the details of the calculations are given elsewhere.²⁹

Electrostatic Theory

LeClaire's theory,⁵ constructed for impurity diffusion in noble metals, calculates the difference between the activation energies for impurity and self-diffusion, $\Delta Q = Q_{imp} - Q_{self}$, on the basis of the electrostatic attraction between a vacancy and an impurity, using the Fermi-Thomas equation. This is the first difficulty in applying this theory to our data; one cannot expect that this equation, which neglects inner electrons and the oscillations of the potential,⁴² should give accurate

TABLE IV. Parameters for diffusion in gamma uranium.

Diffusing element	Activation energy (kcal/mole)	D_0 (cm ² /sec)
U	26.7 ±0.97	1.19 _{-0.40} ^{+0.62} × 10 ^{-3a}
Cr	24.46 ±0.43	5.47 _{-0.87} ^{+1.04} × 10 ⁻³
Mn	13.88 ±1.66	1.81 _{-0.94} ^{+1.96} × 10 ⁻⁴
Fe	12.01 ±0.34	2.69 _{-0.37} ^{+0.48} × 10 ⁻⁴
Co	12.57 ±0.58	3.51 _{-0.76} ^{+0.96} × 10 ⁻⁴
Ni	15.66 ±0.35	5.36 _{-0.74} ^{+0.86} × 10 ⁻⁴
Cu	24.06 ±0.40	1.96 _{-0.30} ^{+0.36} × 10 ⁻³
Nb	39.65 ±0.50	4.87 _{-0.94} ^{+1.18} × 10 ⁻²

* Least-squares fit of the data of Refs. 15-17.

values of the electrostatic potential in γ -U. A further difficulty is encountered in calculating the "screening parameter," q , since this is obtained from the density of states at the Fermi level, $N(E_m)$:

$$q^2 = 4N(E_m). \tag{5}$$

If one takes Friedel's picture of the band structure of γ -U,⁴³ the screening parameter becomes very large, and the electrostatic contributions to ΔQ are of the order of 10⁻⁵ kcal/mol. If one assumes that only the one 7s electron is screening, the screening parameter becomes smaller and the contributions to ΔQ , i.e., the binding energy, the change in the energy of vacancy motion, and the temperature dependence of the correlation coefficient, are of the right order of magnitude.

Another difficulty in the calculation is estimating the "excess valence" of the transition metal impurities in γ -U. In order to get agreement with the experimental data, these were taken as +1 for Cr and Cu, +2 for Mn and Ni, +3 for Fe and Co, and -1 for Nb. These valences are not unreasonable, although there are no other data to support or reject them. Using a value of 1 Å⁻¹ for q and the above valences, fairly good agreement was obtained between ΔQ (theoretical) and ΔQ (experimental). There were, however, severe internal inconsistencies in the calculations. For Co and Fe, the change in the activation energy for motion was negative as expected, but so large that the activation energy for a Co- (or Fe-) vacancy interchange was negative, and ΔQ became reasonable only because the temperature dependence of the correlation coefficient was also large and negative. The negative activation energy could probably have been made positive by adjusting q a little, since the calculation is very sensitive to q , but we feel that this would be a useless exercise unless the new value of q were based on a better knowledge of the band structure of γ -U. An interesting result of these calculations is that a very strong correlation between the directions of successive vacancy jumps can be expected for the diffusion of Co and Fe in γ -U.

³⁹ L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals* (McGraw-Hill Book Company, Inc., New York, 1953), p. 61. These are the radii for CN12; since the hole has tetrahedral coordination, they should be reduced by 12% (*ibid.* p. 49), which still leaves them much larger than the holes in the γ -U lattice.

⁴⁰ W. Hume-Rothery and G. V. Raynor, *The Structure of Metals and Alloys* (Institute of Metals, London, 1954), p. 58.

⁴¹ R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **129**, 1533 (1963).

⁴² J. Friedel, *Advan. Phys.* **3**, 446 (1954).

⁴³ J. Friedel, *Phys. Chem. Solids* **1**, 175 (1956).

Elastic and Thermodynamic Theories

Comparison of our data with Swalin's theory,⁴⁴ which is based on the combined effects of atomic size and elastic properties, is made difficult by the absence of reliable measurements of the elastic properties of γ -U. The activation energy for diffusion definitely does not vary systematically with either atomic size or bulk modulus of the solute. There is some evidence for a size effect, since Au,²¹ which has the same outer electronic structure as Cu and a much larger atomic radius (1.439 Å as opposed to 1.276 Å), diffuses much more slowly and with a higher activation energy than Cu. The agreement with the thermodynamic theory of Turnbull and Hoffman⁴⁵ is also poor, but the calculation is again hampered by the inaccuracy of the binding energies, etc., in the literature.

The Effect of Solutes on Self-Diffusion in γ -U

The ratio $D_{\text{Co}}/D_{\text{self}}$ in gamma uranium is 500 near the β - γ transformation temperature and about 100 at 950°C, indicating a fairly high binding energy between Co atoms and vacancies. In order for Co to diffuse rapidly, the jumping rate of U atoms neighboring the Co atom must increase, i.e., the successive jumps of the vacancy must be strongly correlated, and this should also appear as a strong acceleration of self-diffusion by alloying additions of Co. Conversely Nb, a slow diffuser, should slow down self-diffusion in γ -U, and this is what was found by Adda *et al.*⁴⁶ If one takes

$$D_{\text{self}}(C) = D^0(1 + bC), \quad (6)$$

where D^0 and $D_{\text{self}}(C)$ are the diffusion coefficients of U in pure U and in an alloy of composition C, respectively, a value of $b=197$ is obtained at 939°C from Fig. 3 for the solute Co. This is five to ten times larger than the b values found for diffusion in Ag.⁴⁷ The points at 822.4°C (Fig. 3) do not lie on a straight line; from the two U-Co alloys one gets $b=714$. We have used these values and modification²⁹ of Lidiard's perturbation theory^{47,48} to calculate the correlation factor f for the diffusion of Co in γ -U. Negative values of f are obtained at 822.4°C, and either negative or very

small positive values at 939.9°C, depending on the form of f used. Thus, Co additions do greatly increase D_{self} in γ -U as predicted from the tracer diffusion results, but a correlation coefficient cannot be calculated from Lidiard's theory.

It should be noted that in bcc metals there are no atoms that are nearest neighbors of both the impurity and the vacancy. In order for vacancy-impurity bonding to exist, it must be assumed that the bonding between the vacancy and the impurity extends to the second nearest neighbor sites.

Comparison with the Literature

The present data do not agree with those of Mossé, Lévy, and Adda⁴⁹ in that the activation energies for the diffusion of Fe, Ni, and Cr in γ -U differ by a factor of 2. The disagreement is perhaps caused by their having measured a chemical D , or because their D 's depend on solid solubilities which are not known with sufficient accuracy. Our data for D_{Nb} agrees with Peterson's and Ogilvie's intrinsic D_{Nb} at 97% U in U-U+10%Nb couples.¹⁹

SUMMARY

There now exist reliable data on self- and impurity diffusion in γ -U, and they indicate that gamma uranium is one of the "anomalous" bcc metals in its diffusion behavior. That diffusion in γ -U takes place by a defect mechanism is clear, and vacancies are the preferred defects because of size considerations, although no clear-cut proof of the vacancy mechanism exists as it does for fcc metals. The details of the interaction between defects and impurities are also not entirely clear. A resolution of these problems awaits either more thorough theoretical work, or critical experiments of the type performed on fcc metals,^{2,39} and the latter do not seem to be experimentally feasible for uranium.

ACKNOWLEDGMENTS

We thank A. D. LeClaire and A. B. Lidiard for helpful discussions, R. F. Peart and G. B. Gibbs for access to their theses, J. J. Hines, M. Essling, J. Gray, Jr., E. Koch, and S. A. Moore for help with the experimental work, and B. Garbow for the two-exponential calculations. L. T. Lloyd kindly reviewed the manuscript.

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⁴⁶ Y. Adda, A. Kirianenko, and M. Bendazzoli, *Compt. Rend.* **253**, 653 (1961).

⁴⁷ A. B. Lidiard, *Phil. Mag.* **5**, 1171 (1960).

⁴⁸ The statistical mechanical calculations are similar to those of G. B. Gibbs [thesis, Reading, 1962 (unpublished)].

⁴⁹ M. Mossé, V. Lévy, and Y. Adda, *Compt. Rend.* **250**, 3171 (1960).

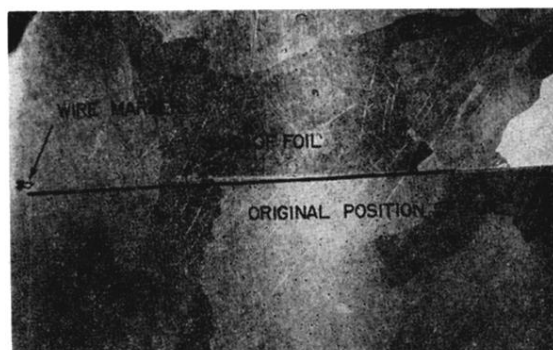


FIG. 4. Kirkendall marker movement during interdiffusion of pure U (bottom) and a U-0.407 at.% Co alloy (top). (Polarized light illumination, 82X.)