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DIFFUSION OF KRYPTON IN RUBIDIUM CHLORIDE AND ITS DEPENDENCE ON RADIATION DAMAGE

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Abstract—The diffusion of krypton in neutron irradiated rubidium chloride was determined by measuring the release of Kr-85m. After negligible irradiation the gas release mechanism corresponded to ideal diffusion. Above 360°C the process was characterized by an activation energy of 10 ± 2 kcal/mole and diffusion by an interstitial mechanism seems probable. Irradiation to high neutron doses resulted in a marked decrease of the measured diffusion coefficient. The healing out of damaged lattice regions was demonstrated as a rapidly increasing krypton release during an isothermal anneal. Possible diffusion mechanisms in the damaged lattice are discussed.

1. INTRODUCTION

INVESTIGATIONS of rare-gas diffusion in solids have for the most part been limited to the release of the fission gases krypton and xenon from nuclear fuels such as UO_2 and UC. The resulting data are of immediate interest for nuclear reactor technology but have hitherto yielded little information for the understanding of diffusion processes. One reason for this may be the complicity of the investigated materials and the difficulties in interpreting the gas release data,[1] and it seems necessary to study less complicated systems in order to obtain basic knowledge of the transport mechanism.

Reports on argon diffusion in potassium and calcium salts show that considerable basic information on the diffusion process may be obtained from neutron-irradiated materials,[2–8] and the present study of krypton diffusion in single crystal RbCl is part of a program initiated with the purpose of learning more about the movement of rare-gas atoms in solids.

2. EXPERIMENTAL PROCEDURE

Single crystal rubidium chloride of optical quality was delivered by Firma Korth in the form of parallelepipedic pieces with approximate dimensions $0{\cdot}5 \times 1 \times 1$ cm. The material contained small amounts of impurities, mainly ions of the alkali and alkaline-earth metals; an analysis showed the presence of 0·01 w/o Na^+, 0·01 w/o K^+, 2×10^{-4} w/o Ca^{2+}, $< 10^{-4}$ w/o Sr^{2+}, and 6×10^{-4} w/o Ba^{2+}.

Irradiation with fast neutrons produces isotopes of krypton according to the reactions

$$Rb^{85}\ (n,p)\ Kr^{85m},\ \text{half life } 4{\cdot}4h$$

and

$$Rb^{87}\ (n,p)\ Kr^{87},\ \text{half life } 78m$$

The naturally abundant rubidium isotopes Rb^{85} and Rb^{87} are present with 72 per cent and 28 per cent respectively, and irradiation in the FR-2 reactor for 10 min at a thermal flux of 3×10^{13} cm^{-2} sec^{-1} (integrated fast flux about 10^{15} cm^{-2}) produces both Kr^{85m} and Kr^{87} in quantities. A gas sample measured one hr after irradiation with the equipment described below gives $1{\cdot}0 \times 10^4$ ipm of Kr^{85m} and $1{\cdot}4 \times 10^3$ ipm of Kr^{87} per gram RbCl; some hours later only Kr^{85m} is measured. Kr^{85} does not seem to be produced directly but only by decay of Kr^{85m}. In order to avoid strongly radioactive specimens the irradiations were performed in 0·1 cm cadmium, thereby suppressing the production of Rb^{86}. However, the creation of S^{35} could not be eliminated in this way as it is produced by fast neutrons:

$$Cl^{35}\ (n,p)\ S^{35},\ \text{half life } 87d$$

After irradiation the specimens were transferred to the annealing apparatus. Briefly, this consisted of a quartz tube containing the single crystal and a thermoelectric couple; the tube was connected to vacuum via an activated charcoal trap. After evacuation of the apparatus the quartz tube was heated with a furnace and the released krypton gas was collected in the trap which was cooled with liquid nitrogen. After a time the charcoal trap was closed and a parallel trap was connected to the system. In this way gas samples were taken with appropriate time intervals, and the krypton content of each trap was transferred into a standard gas container fitted with

a 14 mg/cm^2 aluminum window allowing the measurement of Kr^{85m} with a proportional counter in a fixed geometric position. Each container was periodically measured giving the typical 4·4h decay after subtraction of the background which was determined after two days and caused by S^{35} and Kr^{85}. At the end of each run the crystal was melted and vaporized in order to release all remaining gas. The activity of each gas sample was compared at a fixed time and the fractional gas release could be calculated as a function of diffusion time.

3. EVALUATION METHOD

The theoretically valid relationship between the fractional gas release F, the diffusion time t, and the diffusion coefficient D has been given by INTHOFF and ZIMEN,[10] and tables of the relevant functions have been published by LAGERWALL and ZIMEN.[11] The ideal relationship may be approximated by the tangent through the origin

$$\phi^2 = 4/\pi(S/V)^2\, Dt \qquad (1)$$

where S/V is the surface-to-volume ratio of the specimen. The function ϕ is reasonably equal to F for values $F < 0{\cdot}25$. At higher values one can introduce a correction factor for F and thereby transform the experimentally determined value of F into ϕ.[3,4] It is thus possible to use equation (1) for all values of F and the diffusion coefficient is easily calculated from the slope of a ϕ^2 versus time plot:

$$D = \pi/4{\cdot}1/(S/V)^2\, \mathrm{d}\phi^2/\mathrm{d}t \qquad (2)$$

Figure 1 shows a typical release curve from a multi-temperature experiment. F^2 as well as ϕ^2 is plotted against time, and the possible variation of the slope of ϕ^2 is taken as probable error for the diffusion coefficient. The variation in temperature is also taken into account and the deviations are shown for each point in the Arrhenius diagram, cf. Fig. 2.

4. RESULTS

Multi-temperature anneals were performed with specimens irradiated to an integrated fast flux of 9×10^{14} cm^{-2} (cf. Fig. 1) and Fig. 2 shows the resulting diffusion coefficients in an Arrhenius diagram. Above 360°C a straight-line relationship is valid:

$$D = D_0 \exp(-Q/RT) \qquad (3)$$

The region below 360°C seems to be governed by a process with an activation energy of the order of 60 kcal/mole. This portion of the curve will be discussed later. Further, a number of single temperature experiments were performed at as low dose as possible (6×10^{13} cm^{-2}). The values of D are in accordance with the values shown in Fig. 2 and are separately plotted in Fig. 3. It is therefore assumed that the line drawn in Fig. 3 corresponds to diffusion in a lattice which is not influenced by radiation damage in such a way that the diffusion of krypton is affected.

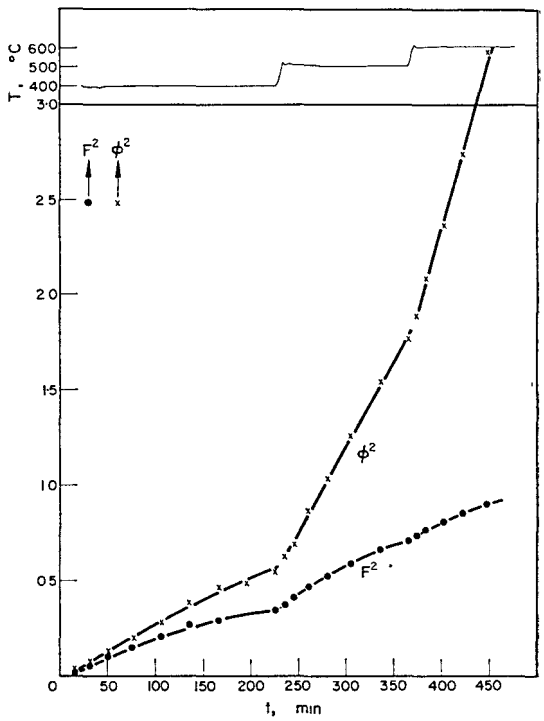

FIG. 1. Release curve from a typical multi-temperature experiment with a specimen irradiated to an integrated fast flux of 9×10^{14} cm^{-2}.

The straight-line relationship above 360°C was calculated whereby all points shown in Figs. 2 and 3 were taken into account:

$$D = 8\times10^{-4} \exp(-9{\cdot}0\times10^3/RT)$$

Considering the fact that most of the multi-temperature experiments shown in Fig. 2 exhibit activation energies of about 11 kcal/mole, values of $\log D_0 = -3{\cdot}1\pm0{\cdot}4$ and $Q = 10\pm2$ kcal/mole may be adopted as good estimations.

Figure 4 shows a multi-temperature anneal with a slightly irradiated crystal; the temperature was first held at 415°C and then raised to 582°C. The crystal was then cooled whereupon the temperature was again kept at 415°C. As is seen from the slope of the ϕ^2 curve of Fig. 4, the diffusion coefficient at 415°C was practically the same though a temperature break at 582°C had been undertaken which indicates an ideal diffusion behaviour. From this experiment an activation energy of 10 kcal/mole was calculated.

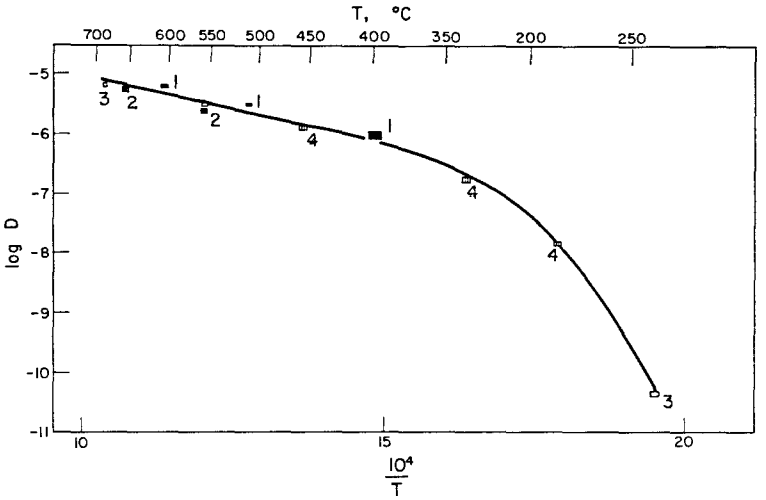

FIG. 2. Arrhenius plot of results from four multi-temperature anneals ($nvt = 9 \times 10^{14}$ cm^{-2}).

As described above, the value of D was not influenced by an increase of the integrated fast flux from 6×10^{13} to 9×10^{14} cm^{-2}. However, a marked influence was observed after irradiation to 5×10^{16} cm^{-2} resulting in an inhibition of the rate of diffusion. Figure 5 shows a multi-temperature anneal and the release characteristics may be noted as follows:

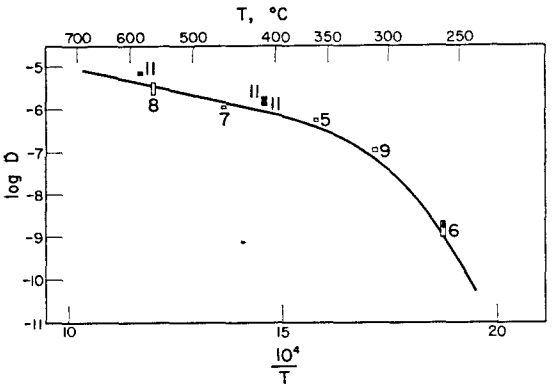

FIG. 3. Arrhenius plot of results from five single temperature anneals (unfilled symbols) and one multi-temperature anneal (filled symbols). The specimens had been irradiated to an integrated fast flux of 6×10^{13} cm^{-2}.

(*a*) In the first stage a temperature of 260°C was maintained and the diffusion coefficient which was of the order of only 10^{-13} cm^2 sec^{-1} showed a tendency to decrease.

(*b*) In the second temperature stage (360°C) the diffusion coefficient increased continuously from $5{\cdot}7 \times 10^{-12}$ to $4{\cdot}4 \times 10^{-10}$ cm^2 sec^{-1}; a constant value was never reached.

(*c*) In the third stage, a temperature of 510°C was kept for only 30 min and a practically constant value of $D = 1{\cdot}3 \times 10^{-6}$ cm^2 sec^{-1} was observed.

(*d*) In the fourth stage the original temperature of 260°C was once more reached and a constant but considerably higher diffusion coefficient was observed, cf. Fig. 6.

(*e*) In the fifth stage 360°C was again maintained whereby the diffusion coefficient quickly increased from 3×10^{-8} cm^2 sec^{-1} to a constant value of about $1{\cdot}3 \times 10^{-7}$ cm^2 sec^{-1}.

(*f*) In the last stage the temperature was kept at 610°C for a short time and a slightly increasing diffusion coefficient was observed.

The results of this experiment are shown in Fig. 6 together with two single temperature anneals at 460°C and 600°C resp.; the latter experiments were performed with crystals irradiated to an integrated fast flux of more than 10^{18} cm^{-2}.

Experimental data for all runs are summarized in Table 1. The resulting diffusion coefficients are satisfactorily reproducible and have evidently

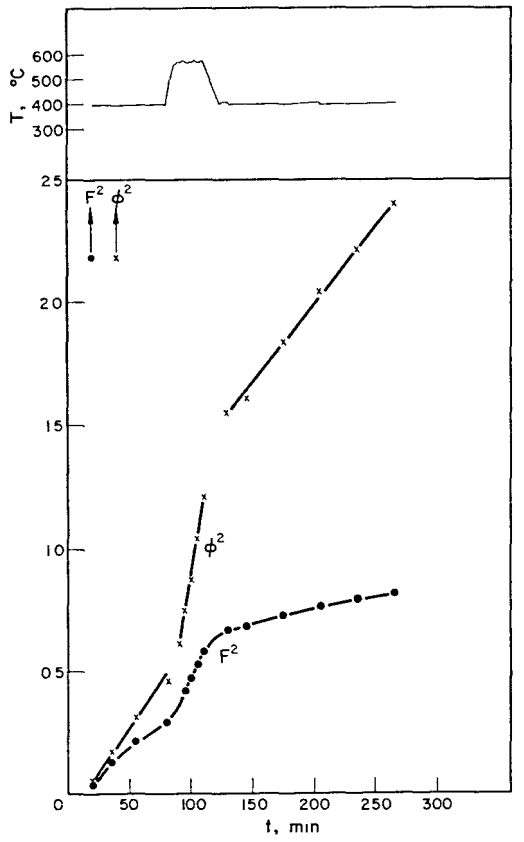

FIG. 4. Release of krypton from a slightly irradiated specimen ($nvt = 6 \times 10^{13}$ cm^{-2}) at 415°C with a temperature break at 582°C.

not been influenced by other gas releasing processes such as vaporization of the specimen.

5. DISCUSSION

One may characterize the release of krypton from rubidium chloride by summarizing the experimental facts:

(*a*) *Low irradiation dose, cf. Fig.* 3

Ideal diffusion kinetics is observed at all temperatures with indications of a slightly increasing diffusion coefficient during an isothermal anneal at the lowest temperatures. Above 360°C a straight line relationship log D vs. $1/T$ was found, corresponding to an activation energy of 10 ± 2 kcal/mole. In the temperature region of 260°C to 360°C low values of D were noted and an activation energy of the order of 60 kcal/mole.

(*b*) *Influence of radiation damage, cf. Fig.* 6

At low temperatures low values of D were observed and there were indications of a slightly decreasing diffusion coefficient during the run. At higher temperatures a marked, continuous increase of D during an isothermal anneal was obvious, cf. Fig. 5. Above about 460°C ideal diffusion kinetics was predominant and values of D were found which are only slightly lower than those at low irradiation dose.

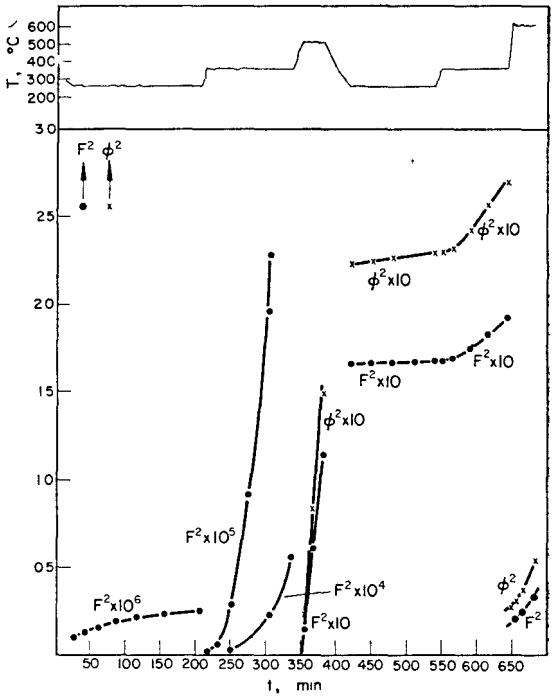

FIG. 5. Release curve demonstrating the influence of radiation damage upon the release of krypton. The specimen was irradiated to an integrated fast flux of 5×10^{16} cm^{-2} and subsequently annealed at five temperature levels; the corresponding diffusion coefficients are shown in Fig. 6 (designation 10a–f).

The rubidium chloride lattice is of the NaCl type and exhibits a Schottky disorder. Though the self-diffusion has not been measured in rubidium chloride, it is reasonable to believe that the lattice ions move in accordance with other

Table 1. *Summary of experimental data*

No.	Dimensions of specimen (cm)	Irradiation nvt* (cm^{-2})	Anneal Temp. (°C)	Anneal Time at temp. (min)
1	$0{\cdot}75 \times 1{\cdot}08 \times 1{\cdot}11$	9×10^{14}	400	210
			510	130
			610	103
2	$0{\cdot}47 \times 1{\cdot}07 \times 1{\cdot}13$	9×10^{14}	560	26
			660	49
3	$0{\cdot}51 \times 1{\cdot}05 \times 1{\cdot}12$	9×10^{14}	240	280
			560	40
			690	50
4	$0{\cdot}52 \times 1{\cdot}06 \times 1{\cdot}17$	9×10^{14}	285	245
			338	120
			460	92
5	$0{\cdot}51 \times 1{\cdot}07 \times 1{\cdot}12$	6×10^{13}	360	270
6	$0{\cdot}53 \times 1{\cdot}07 \times 1{\cdot}12$	6×10^{13}	260	330
7	$0{\cdot}52 \times 1{\cdot}06 \times 1{\cdot}13$	6×10^{13}	460	240
8	$0{\cdot}56 \times 1{\cdot}07 \times 1{\cdot}15$	6×10^{13}	560	237
9	$0{\cdot}51 \times 1{\cdot}07 \times 1{\cdot}12$	6×10^{13}	310	330
10	$0{\cdot}53 \times 1{\cdot}08 \times 1{\cdot}19$	$5{\cdot}0 \times 10^{16}$	260	190
			360	119
			510	30
			260	120
			360	92
			610	30
11	$0{\cdot}53 \times 1{\cdot}07 \times 1{\cdot}18$	6×10^{13}	415	40
			582	20
			415	135
12	$0{\cdot}56 \times 1{\cdot}10 \times 1{\cdot}16$	$1{\cdot}2 \times 10^{18}$	595	423
13	$0{\cdot}50 \times 1{\cdot}07 \times 1{\cdot}17$	$1{\cdot}6 \times 10^{18}$	460	510

* The fast flux information is based on measurement of Si31, whereby a cross section of 30mb was assumed for the reaction P31 (n, p) Si31. The thermal flux was about 20 times higher than the fast one.

alkali halides, e.g. a vacancy mechanism is governing the self-diffusion which proceeds with an activation energy of the order of 50 kcal/mole for cations and with still higher values for anions. As the krypton release at higher temperatures is characterized by ideal diffusion kinetics with high diffusion coefficient and a surprisingly low activation energy, one is obliged to assume that the rare-gas atoms do not make use of a vacancy mechanism for their movements in the lattice. The only possibility is diffusion by an interstitial mechanism or movement along lattice defects of various kinds.

However, the influence of radiation damage upon the diffusion at lower temperatures is such as to make an interstitial diffusion mechanism seem unlikely as sole process in the damaged lattice. After irradiation to higher doses the diffusion coefficient is lowered with many orders of magnitude and during an isothermal anneal the diffusion coefficient is continuously increasing, indicating a healing out of the radiation damage. A damaged lattice still contains enough interstitial paths to permit practically free movement of the rare-gas atoms and one must conclude that the diffusing krypton atoms in some way associate with the created lattice defects and are thus more or less immobilized. As the value of D is dependent on the irradiation dose the rare-gas atoms do not create these defects themselves and the formation of micro-bubbles by random encounter is improbable considering the low concentration of krypton which for the experiment shown in Fig. 6

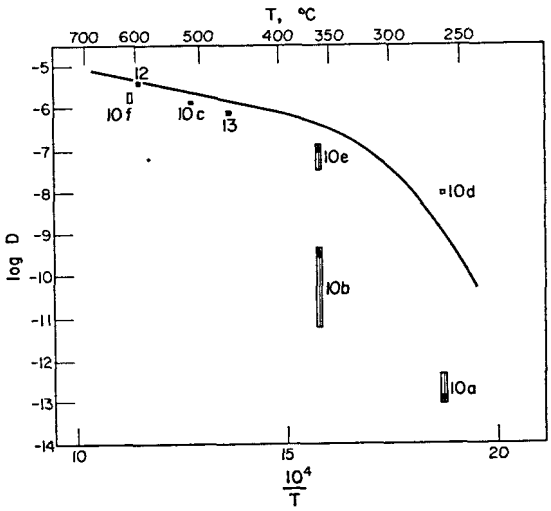

FIG. 6. Arrhenius plot of the results from specimens damaged by radiation; the drawn line corresponds to the diffusion coefficient in the undisturbed lattice.

is certainly less than 10^{10} atoms/cm^3. The existence of rare-gas traps has been discussed by HURST[12] and others[13]; the well-known phenomenon of bubble formation could be a late stage of trapping,[14] and LAGERWALL[4,5] has proposed that vacancy clusters constitute such sinks in CaF_2.

Without trying to identify the physical nature of these irradiation-induced defects, one may think of the entity krypton/defect as being formed at an early stage of the post-activation diffusion anneal and as being immobile or diffusing at a very low rate (Fig. 5, 1st temperature stage). At higher temperatures the healing out process is measurably influencing the diffusion which means that either the diffusing entity is reducing in size or the krypton atom is breaking away, resulting in a continuous increase of the diffusion coefficient (Fig. 5, 2nd temperature stage). Though one feels that the latter mechanism is the most plausible one, it is not possible to say which process occurs at the present state of knowledge, only that it is connected with its own kinetics. Figure 7 shows this healing process as a straight line in a $\sqrt{(F)}$ vs. t plot.

Considering the influence of radiation damage and the fact that this damage is only partly healed out during an isothermal anneal, one may ask oneself how significant the measured activation energy of 10 kcal/mole is and if the lowered diffusion coefficient in the region below 360°C is also a result of radiation damage, cf. Fig. 3. The result of the experiment shown in Fig. 4 indicates that the slope above 360°C is really the one which corresponds to diffusion in an undisturbed lattice. The region below 360°C is still a matter of question and the present investigation does not produce enough information to determine the diffusion mechanism.

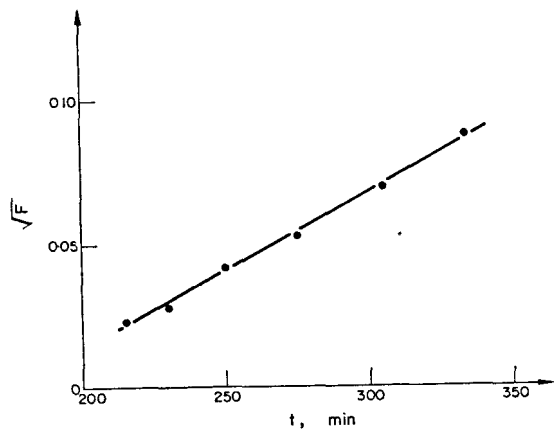

FIG. 7. Healing out of damaged lattice regions, demonstrated as a rapidly increasing krypton release during an isothermal anneal; the plot corresponds to the second temperature stage of Fig. 5.

It has been shown that the system Ar/KCl is even more sensitive to radiation damage than is Kr/RbCl,[9] and investigations of irradiation sensitive diffusion and its causes are now continued on single crystal KCl.

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