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P. Schmeling

GESELLSCHAFT FÜR KERNFORSCHUNG M.B.H.
KARLSRUHE

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Institut für Radiochemie, Kernforschungszentrum Karlsruhe

Influence of Radiation Damage upon the Diffusion of Argon in Potassium Chloride

By

P. SCHMELING

The diffusion of Ar^{41} and Ar^{39} in single crystals of potassium chloride is studied as a function of irradiation dose. It is found that the diffusion coefficients of argon are significantly decreased by increasing the irradiation dose. The influence of neutron bombardment is considerable at low temperatures, the diffusion coefficient being changed by several orders of magnitude. The general behaviour, as shown in an Arrhenius diagram, follows the same pattern independently of the irradiation dose. At high temperatures the diffusion coefficient is constant with time and has an activation energy of 8.7 ± 0.8 kcal/mol and an interstitial diffusion mechanism seems to be plausible. At intermediate temperatures the diffusion coefficient increases during isothermal annealing and ultimately reaches a constant value. At low temperature the diffusion coefficient is again constant with time.

Die Diffusion von Ar^{41} und Ar^{39} in Einkristallen von Kaliumchlorid wurde als Funktion der Bestrahlungsdosis untersucht. Es stellte sich heraus, daß der Diffusionskoeffizient von Argon mit steigender Bestrahlungsdosis beträchtlich abnimmt. Dieser Einfluß war besonders deutlich bei tieferen Temperaturen, wo der Diffusionskoeffizient sich um mehrere Größenordnungen änderte. Die Darstellung des Diffusionskoeffizienten im Arrheniusdiagramm zeigt denselben prinzipiellen Verlauf unabhängig von der Bestrahlungsdosis. Bei höheren Temperaturen wurden zeitlich konstante Diffusionskoeffizienten beobachtet; die Aktivierungsenergie betrug $8{,}7 \pm 0{,}8$ kcal/mol, ein Zwischengittermechanismus erscheint plausibel. Bei mittleren Temperaturen stieg der Diffusionskoeffizient während eines isothermen Versuches an und erreichte schließlich einen konstanten Wert. Bei tiefen Temperaturen war der Diffusionskoeffizient wieder zeitlich konstant.

1. Introduction

In recent years the question of rare-gas movement in solids has aroused much interest for the interpretation of the physical changes of a body under neutron or charged particle bombardment. Few investigations have been performed with the aim of studying the basic mechanisms controlling the diffusion of rare-gases in solids, and the attention has been focused on bubble formation and bubble movement in metals. Lately the diffusion of rare-gases in ionic crystals has been successfully studied [1 to 8] and in one case Lagerwall [4] has shown that the diffusion of argon in calcium fluoride proceeds according to an interstitial mechanism.

The influence of radiation damage on the diffusion properties has in no case been systematically investigated, and the experimental results presented here on argon diffusion in potassium chloride have been performed in order to show that such an influence exists and is important for the interpretation of the diffusion mechanism.

2. Experimental Procedure

Parallelepipedic pieces of single crystal potassium chloride of optical quality were used; the content of barium, calcium, and strontium was about 10^{-3} wt/o. The specimens were irradiated in 0.1 cm cadmium in order to suppress the creation of K^{42} by thermal neutrons. Fast neutrons produce isotopes of argon according to

$$K^{39}(n, p)Ar^{39}, \text{ half life } 265 \text{ y },$$

and

$$K^{41}(n, p)Ar^{41}, \text{ half life } 110 \text{ min } .$$

Irradiation in the FR2 reactor for 10 min in a fission flux of 1.5×10^{12} cm^{-2} s^{-1} (integrated fast dose[1]) about 10^{15} cm^{-2}) produced negligable amounts of Ar^{39}; a gas sample measured one hour after irradiation gave 4×10^5 ipm per gram KCl, and irradiation times as short as 6 s still yielded enough Ar^{41} to make a diffusion experiment possible. Irradiation for two weeks (integrated fast dose about 10^{18} cm^{-2}) produced amounts of Ar^{39} as well, a gas sample measured one hour after irradiation gave 9×10^4 ipm of Ar^{39} and 5×10^6 ipm of Ar^{41} per gram KCl.

The irradiated crystals were annealed in vacuum. The technique of measuring rare-gas release has been adequately described previously and requires no detailed discussion here [9, 10].

3. Evaluation Method

The experimentally measured quantities are the fractional gas release F at the temperature T and the diffusion time t. The relationship between F, t, and the diffusion coefficient D has been given by Inthoff and Zimen [11]; for the diffusion from a parallelepipedic specimen with the dimensions $a_1 \times a_2 \times a_3$ equation (1) is valid

$$F = 1 - \Sigma(a_1) \cdot \Sigma(a_2) \cdot \Sigma(a_3) \,, \tag{1}$$

where $\Sigma(a_i) = \sum_{n=0}^{\infty} 8\,(2\,n + 1)^{-2}\,\pi^{-2} \exp\left[-\,(2\,n + 1)^2\,\pi^2\,D\,t/a_i^2\right]$.

Tables and graphs of the solved functions have been published by Lagerwall and Zimen [12], and Lagerwall [3, 4] has introduced a correction factor for F, thereby transforming F^2 into the function φ^2. From the slope $\mathrm{d}\varphi^2/\mathrm{d}t$ in a φ^2-t-plot the diffusion coefficient is easily calculated

$$D = \pi/4\,(S/V)^{-2}\,\mathrm{d}\varphi^2/\mathrm{d}t \,, \tag{2}$$

where S/V is the surface-to-volume ratio of the specimen.

The ideal kinectics is demonstrated by the linearity of a φ^2-t-plot and Fig. 1 exemplifies this noticeably reproducible behaviour. Fig. 2 shows a typical multitemperature anneal, and the linearity of φ^2 at constant temperature is obvious. Release experiments during which the temperature was continuously increased from low values to the melting point were also performed. The result is a continuously increasing release of rare-gas as is demonstrated in Fig. 3. The release curve can be evaluated under the assumption that the gas release at every moment is in equilibrium with the specimen temperature. The diffusion coefficient at any temperature was thus calculated from the slope of the φ^2/t-curve. The advantage of this procedure is that values of D are obtained over the whole temperature range; it will be shown later that the resulting diffusion coefficients are representative for the diffusion behaviour.

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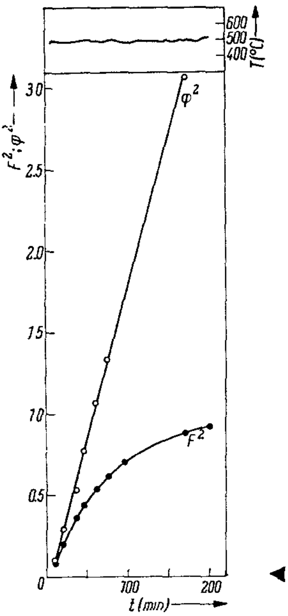
[1] The fast dose data are based on measurement of Si^{31}, whereby a cross section of 30 mb was assumed for the reaction P^{31} (n, p) Si^{31}, and are valid for a fission spectrum.



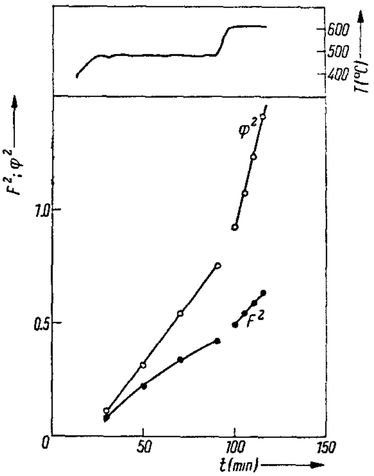


Fig. 2. Release curve (Ar^{41}) from a typical multi-temperature experiment; the specimen ($0.53 \times 1.05 \times 1.09$ cm^3) had been irradiated to an integrated fast dose of 9×10^{12} cm^{-2}

◀ Fig. 1. Release curve (Ar^{41}) from typical single-temperature experiment; the specimen ($0.53 \times 0.99 \times 1.09$ cm^3) had been irradiated to an integrated fast dose of 9×10^{14} cm^{-2}

4. Results

4.1 Experiments performed while continuously increasing the temperature

During the anneals while continuously increasing the temperature gas samples were taken every 50 °C. The variation of F^2 and φ^2 with temperature is plotted according to Fig. 3, from which the diffusion coefficients are calculated. The resulting Arrhenius plot is shown in Fig. 4 for four different experiments,

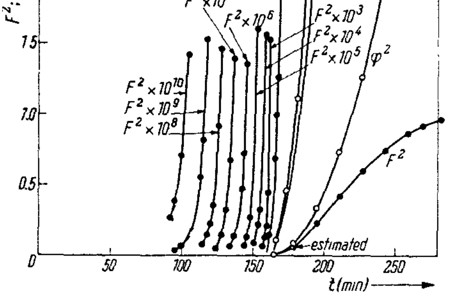


Fig. 3. Typical release curve (Ar^{41}) from an experiment with continuously increased temperature; the specimen ($0.53 \times 1.05 \times 1.09$ cm^3) had been irradiated to an integrated fast dose of 5×10^{16} cm^{-2}

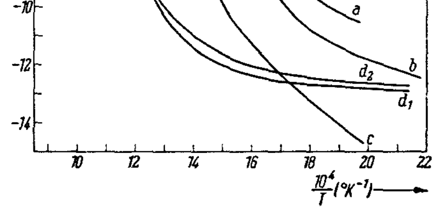


Fig. 4. Arrhenius plot of results from four experiments with continuously increased temperature after irradiation to an integrated fast dose of a) 9×10^{13} cm^{-2}, b) 9×10^{14} cm^{-2}, c) 5×10^{15} cm^{-2}, and d) 1.2×10^{18} cm^{-2} (d_1 refers to the measurement of Ar^{41} and d_2 to Ar^{39}, from the same specimen)

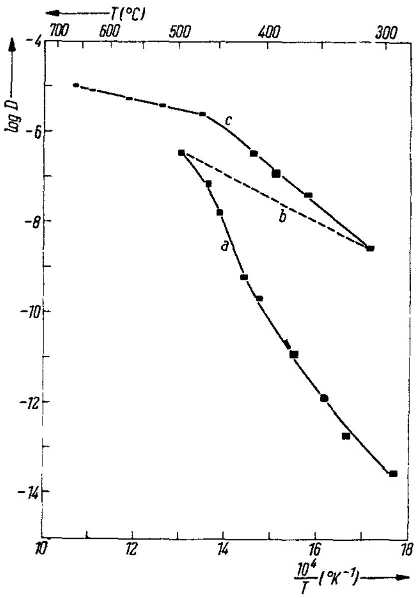


Fig. 5. Arrhenius plot of results from an experiment in which the temperature was slowly raised from a) room temperature to 500 °C and b) quickly lowered to room temperature. The temperature was again raised, from c) room temperature to the melting point. The specimen ($0.47 \times 1.00 \times 1.08$ cm^3) had been irradiated to an integrated fast dose of 5×10^{16} cm^{-2}

each performed with specimens irradiated to different neutron doses. One important conclusion of these experiments is that the presence of radiation damage strongly affects the value of D. Further, the damage received at high irradiation dose seems to heal out at a slow rate as the values of D from the various experiments coincide only at high temperature. With lowered dose the values of D coincide at high temperature, indicating an activation energy of about 10 kcal/mol above 450 °C and low irradiation dose. Precise calculation of the activation energy were made on basis of isothermal anneals which will be described later.

The healing out of radiation damage is further exemplified in the Arrhenius diagram of Fig. 5. The temperature was first continuously raised to 500 °C, whereupon the specimen was cooled down and the temperature increased to the melting point. The second annealing stage exhibits diffusion coefficients which are 2 to 5 orders of magnitude larger than in the first stage.

4.2 *Single and multi-temperature experiments*

Typical gas release in single and multi-temperature experiments are shown in Fig. 1 and Fig. 2. At enough high a temperature the straight line relationship of the φ^2-t-plot is preserved, indicating an ideal diffusion mechanism. The behaviour at low temperature is more complicated and will be discussed later.

4.21 *Diffusion after irradiation to low dose*

Fig. 6 shows that the diffusion coefficients measured in isothermal anneals after irradiation to 9×10^{13} cm^{-2} coincide above 400 °C with the values obtained in the experiment with continuously increasing temperature (see Fig. 4a). The relationship at 400 to 760 °C is given by

$$D = 1.3 \times 10^{-3} \exp\,(-\,9.5 \times 10^3/R\,T)\,. \qquad (3)$$

In the temperature region of 280 to 400 °C the release curves exhibit a non-ideal kinetics, in accordance with the findings reported by Richter and Zimen [7]. A typical behaviour is shown in Fig. 7. The diffusion coefficient apparently increases during the isothermal anneal and reaches a constant value after a certain time at the temperature. This ultimate value of D coincides with the extrapolated straight line of equation (3) only at temperatures near but not much below 400 °C; as is shown in Fig. 6, the ultimately reached value of D is mostly well below the extrapolated line. An increase of D was not observed at temperatures as low as 250 °C.

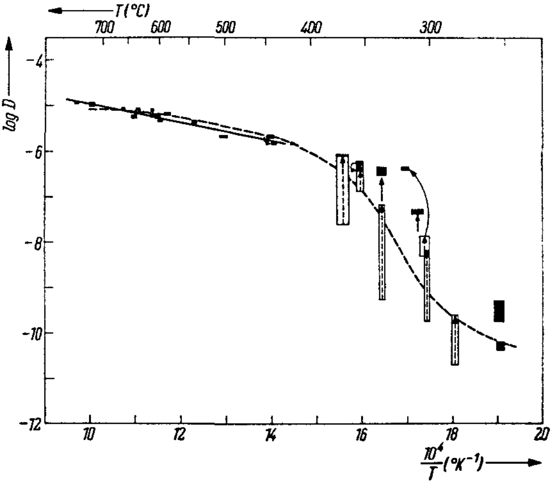


Fig. 6. Arrhenius plot of results (Ar^{41}) from single and multi-temperature experiments after irradiation to an integrated fast dose of 9×10^{13} cm^{-2}. The broken line is the same one as in Fig. 4a. Filled points represent constant diffusion coefficients, broken arrows indicate that D has increased during an isothermal anneal; full arrows show the value of D after heat treatment for 10 to 15 min at 600 °C. The full line takes all points above 440° into consideration, cf. equation (3)

The slope of (3) was further checked in the following way, see Fig. 8. The specimen was held at 444 °C; the temperature was then increased to 610 °C for 13 min whereupon the crystal was cooled down and the anneal could proceed at 440 °C. The diffusion coefficient was practically the same though a temperature break to 610 °C had been undertaken (see Fig. 6), indicating that the values of D at and above 440 °C are not affected by the healing out phenomena at lower temperatures described above. A temperature break to about 600 °C for 10 to 15 min does, however, affect the values of D at lower temperatures as indicated by the arrows in Fig. 6. A treatment at 600 °C seems to accelerate

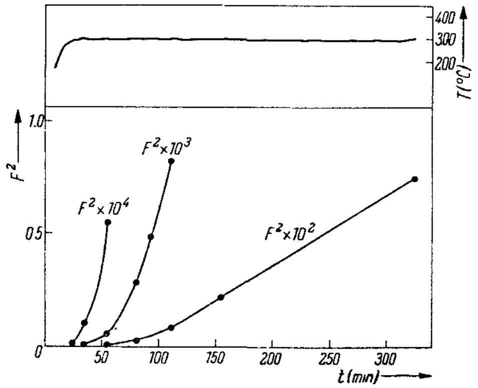


Fig. 7. Release curve (Ar^{41}) exhibiting a continuous increase of the observed diffusion coefficient during an isothermal anneal at 302 °C; the specimen (0.49 × 0.99 × 1.00 cm^3) had been irradiated to an integrated fast dose of 9×10^{13} cm^{-2}

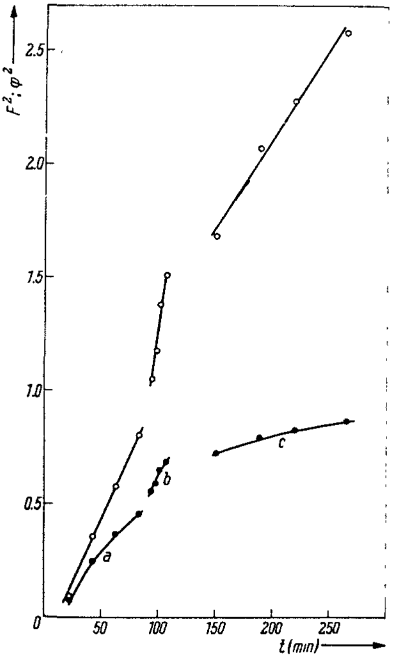


Fig. 8. Release of Ar^{41} at a) 444 °C with b) a temperature break for 13 min at 610 °C; after cooling the anneal was continued at c) 440 °C. The specimen (0.42 × 1.00 × 1.05 cm^3) had been irradiated to an integrated fast dose of 9×10^{13} cm^{-2} ▶

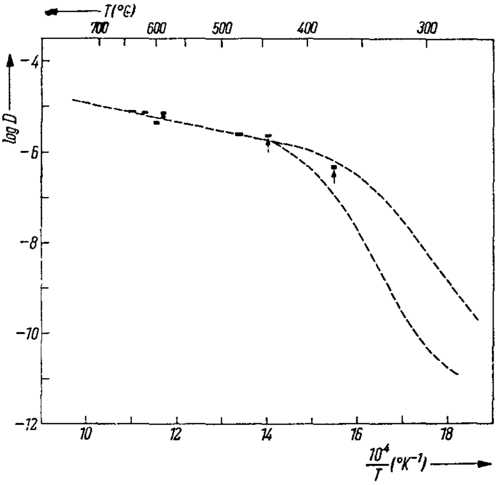


Fig. 9. Arrhenius plot of results (Ar^{41}) from multi-temperature experiments after irradiation to an integrated fast dose of 9×10^{12} cm^{-2}. The broken lines correspond to the diffusion coefficient measured after 9×10^{13} cm^{-2}, cf. Fig. 6. Arrows show the value of D after a heat treatment at temperatures above 590 °C for about 15 min. The broken line represents the best fit above 440 °C to equation (4) as well

the process of increasing diffusion coefficient shown in Fig. 7, and the ultimate values of D are close to the extrapolated line of (3). This behaviour is at best studied with heavily irradiated crystals.

Further, a number of experiments were performed with crystals irradiated for 6 s corresponding to an integrated fast dose of only 9×10^{12} cm^{-2}. The results of these experiments, as shown in Fig. 9, agree with those described above. A variation of the irradiation dose at this irradiation level (10^{13} to 10^{14} cm^{-2}) does not seem to affect the diffusion coefficient of argon to a measurable degree. The best line fitting the points above 400 °C has the equation

$$D = 9.5\times10^{-4} \exp\left(-\,8.7\times10^{3}/R\,T\right). \tag{4}$$

As is seen from Fig. 4 the diffusion coefficients seem to coincide above about 450 °C even if the integrated fast dose is varied from 10^{13} to 10^{15} cm^{-2}. This

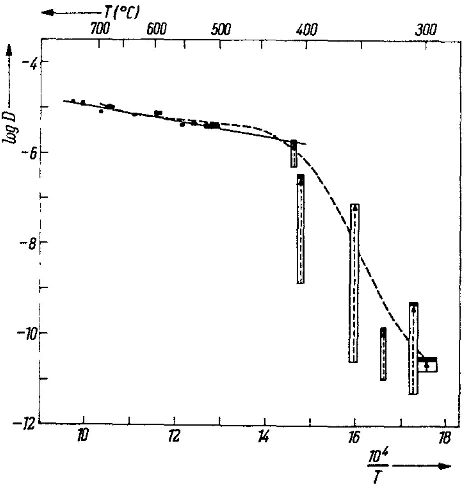


Fig. 10. Arrhenius plot results (Ar^{41}) from multi-temperature experiments after irradiation to an integrated fast dose of 9×10^{14} cm^{-2}. The broken line is the same one as in Fig. 4b; broken arrows indicate that D has changed during an isothermal anneal. The full line takes all points above 500 °C into consideration, cf. equation (5)

was verified by performing a number of experiments after irradiation to 9×10^{14} cm^{-2}; the best equation fitting the points of Fig. 10 above 500 °C is

$$D = 5.8 \times 10^{-4} \exp(-7.9 \times 10^3/R\,T)\,. \tag{5}$$

Equations (3), (4), and (5) may be regarded as examples of the variation of $\log D_0$ and Q, and the mean values of $\log D_0 = -3.1 \pm 0.2$ and $Q = 8.7 \pm \pm 0.8$ kcal/mol are here regarded as representative for the diffusion at temperatures above 400 °C after irradiation to low doses.

4.22 Diffusion after irradiation to comparatively high doses

Changing the integrated fast dose from 10^{15} to 10^{18} cm^{-2} changes the measured diffusion coefficient considerably, a decrease in D of many orders of magnitude is frequent as is seen from Fig. 11. At high irradiation dose not only Ar^{41} but

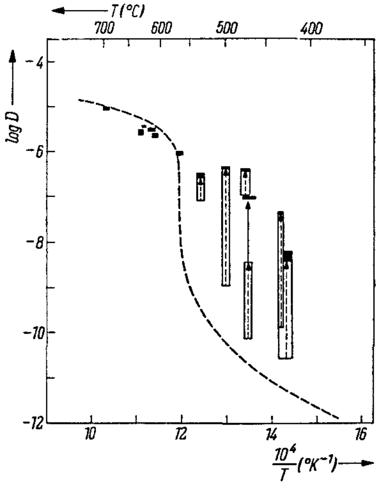


Fig. 11. Arrhenius plot of results from single and multi-temperature experiments after irradiation to an integrated fast dose of about 10^{18} cm^{-2}. The dashed line is the same one as in Fig. 4d; designation as in Fig. 6

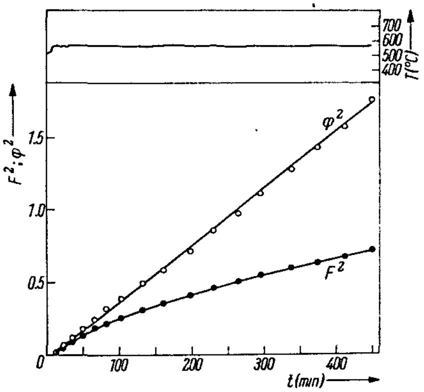


Fig. 12. Release curve (Ar^{41}) after irradiation to an integrated fast dose of 1.6×10^{18} cm^{-2}. The specimen had the dimensions $0.55 \times 1.05 \times 1.07$ cm^3

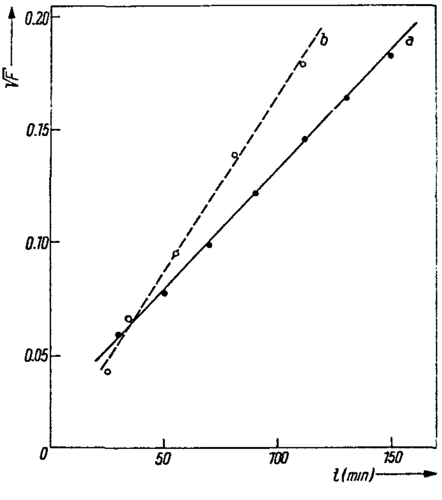


Fig. 13. Release curve from an isothermal anneal demonstrating a continuous increase of the apparent diffusion coefficient.

a) specimen irradiated to an integrated fast dose of 1.6×10^{18} cm^{-2}, annealed at 471 °C

b) specimen irradiated to an integrated fast dose of 9×10^{13} cm^{-2}, annealed at 302 °C; the complete release curve is shown in Fig. 7

also Ar^{39} is produced in quantities, and as expected both isotopes show approximately the same diffusion coefficients.

Only at temperatures in the neighbourhood of 700 °C do the diffusion coefficients coincide with those measured at low irradiation dose. At lower temperatures, but still above 550 °, the release seems also to be ideal in accordance with Fig. 12, though the values of D are considerably lowered and seem to indicate an activation energy of about 30 kcal/mol.

At still lower temperatures (400 to 550 °C) the same non-ideal release pattern was observed as with slightly irradiated crystals in the region of 280 to 400°, cf. Fig. 7. The value of D increased continuously during an isothermal anneal and reached an ultimate value many orders of magnitude lower than the corresponding values for slightly irradiated crystals. The increase of D with time seems to follow its own kinetics; Fig. 13 shows that the release F is proportional to the second power of t during the first part of the anneal. However, the ultimately reached value of D did not seem to be reproducible and there were indications that the time required to reach constant temperature influenced the process.

5. Discussion

5.1 Comparison with other investigators

A comparison with other investigations has to be made with caution as the radiation damage received by the specimens influenced the results, a fact which has hitherto been overlooked. To this comes the difficulties in estimating this influence from reported thermal neutron data as the fast neutrons are responsible for the damage. With these objections in mind it may be illustrative to review the work done by other investigators, cf. Fig. 14.

The measurements of argon diffusion in KCl published by Kalbitzer [1] were made with specimens irradiated to a dose comparable with the highest one reported here and it is therefore not surprising that an activation energy as high as 41 kcal/mol was found. Non-ideal gas release was observed at 107 °C; a continuously increasing value of D during an isothermal anneal was not reported

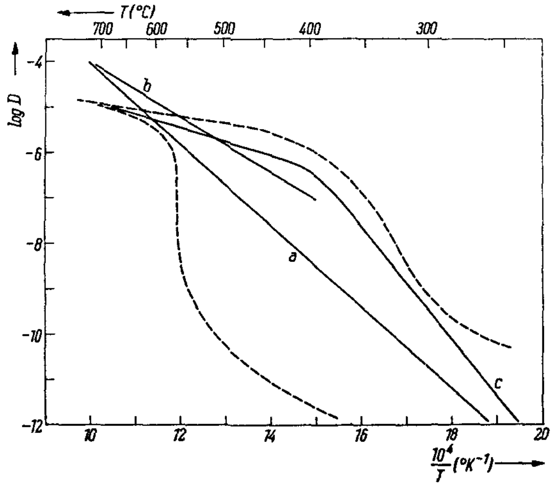


Fig. 14. Diffusion of argon in KCl as measured by various investigators.

a) Kalbitzer [1], integrated thermal dose 10^{19} cm^{-2}; b) Matzke [5], integrated thermal dose 4.2×10^{19} cm^{-2}; c) Richter and Zimen [7], integrated fast dose 10^{15} to 10^{17} cm^{-2}. The broken lines show the limits of D for specimens irradiated to various doses according to the present investigation though it was found that higher values were obtained if the irradiated specimen was pre-treated at a high temperature.

Matzke [5] also irradiated KCl single crystals to a dose comparable with the highest one reported here. The release of Ar^{39} was found to be ideal at temperatures above 400 °C, giving an activation energy of 26 kcal/mol. Below 400 °C the release was non-ideal, indicating low values of D.

Richter and Zimen [7] measured the diffusion in KCl single crystals irradiated to an integrated fast dose of 10^{15} to 10^{17} cm^{-2}. As is shown in Fig. 14, their results are in accordance with the ones reported here. Above 400 °C the activation energy was found to be 0.6 eV (11 kcal/mol), at lower temperatures the values of D varied and an activation energy of 2.4 eV (53 kcal/mol) was estimated.

5.2 *Mechanism of argon diffusion*

Regardless of the irradiation dose, the diffusion behaviour changes with temperature according to the same pattern. In the temperature region I (highest temperature) the diffusion coefficient is constant with time, e. g. the release kinetics is ideal. In the region II (intermediate temperature) the value of D increases during an isothermal anneal and ultimately reaches a constant value. In the region III (low temperature) the diffusion coefficient has a low value and the release kinetics is ideal. The temperature limits corresponding to a certain temperature region varies with the irradiation dose.

This general behaviour is not restricted to potassium chloride as other alkali halides show similar release characteristics. The presence of the three temperature regions is established in the case of krypton diffusion in rubidium chloride [8] and a similar behaviour is reported for argon diffusion in potassium bromide [7].

From measurements of the self-diffusion coefficients it is known that the energy changes associated with the vacancy jump process is well above 30 kcal/mol [13]. The energy E_s for the creation df a Schottky defect in KBl is known to be 48 kcal/mol. The energy of migration of any impurity atom in this lattice has therefore to be $> 1/2\ E_s$ if the atom migrates by a vacancy mechanism in the intrinsic range. As the activation energy found at high temperatures (region I) is only 8.7 kcal/mol for argon diffusion, a vacancy mechanism must be excluded.

It therefore seems probable that the argon diffuses according to an interstitial mechanism at high temperatures. The diffusion mechanism at lower temperatures (region II and III) is apparently complicated; hesitating to base a conclusion on scanty evidence, a further discussion of the diffusion mechanism at low temperatures is here avoided until more experimental data are available. The investigations will continue with the aim of learning more about the movement of rare-gas atoms in a damaged ionic lattice.

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