

SELF-DIFFUSION IN SOLID KRYPTON

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Tracer diffusion in solid krypton has been measured in the temperature range $90^\circ < T < 115^\circ\text{K}$ by means of an isotopic exchange technique. The diffusion parameters obtained are in reasonable accord with values estimated from data for other rare-gas solids through the principle of corresponding states. The addition of a small amount of O_2 ($\sim 0.4\%$) appears to depress the diffusion of the krypton.

Thermodynamic properties of rare-gas solids (heat capacity,^{1,5} thermal expansion,⁶⁻⁸ and compressibility⁷⁻⁹) have been measured recently and the results compared with those calculated for simple models (e.g., two-body forces and Lennard-Jones-type interatomic potential). Similar experimental-theoretical comparisons have been made for the formation^{6,10-12} and migration^{11,13-15} of point defects in these solids. While the inclusion of many-body forces may be needed to account for some of the results,⁶ more extensive experimental data, particularly of atomic transport, are clearly desirable to test the proposition.

In this Letter, we report the main results from the measurement of tracer diffusion in solid krypton. Diffusion in this solid has not been measured hitherto. Since a convenient radioisotope ^{85}Kr was readily available, an isotopic exchange technique was developed. This experimental method has the particular advantage that it can be used over a relatively wide temperature range and that a series of measurements at different temperatures can be made on the same specimen. A full description of the method, together with the detailed results, will be published elsewhere.

The diffusion specimens (1.3-9.7 g) were grown from Matheson Research Grade krypton (total impurities after the diffusion experiments ≤ 150 ppm) to which ^{85}Kr was added. The krypton was condensed at about 2° above its triple point (115.8°K) into a cylindrical brass container with conical bottom that was mounted in a low-temperature cryostat. Fusion was effected by conducting heat away from the bottom of the container by means of a thin copper wire. The technique of crystal growth was therefore essentially that developed by Bridgmann. When crystallization was complete, the specimens were annealed for 48 h at 113°K and subsequently cooled to the starting temperature of the diffusion experiment at rates between 0.005 and 0.01° per min. Krypton vapor was then circulated continuously over the solid

specimen and the change in radioactivity of the vapor measured with a solid-state detector.

If isotopic exchange at the surface of the crystal is rapid compared with diffusion within, the boundary conditions for the experiment lead to the following expression for the time dependence of the exchange between the crystal and its vapor:

$$\frac{dn^2}{dt} = \frac{4A^2C_0^2D^*}{\pi} \quad (1)$$

Here n is the number of ^{85}Kr atoms in the gas phase at time t , A the surface area of the solid, C_0 the initial concentration of ^{85}Kr in the solid, and D^* the tracer diffusion coefficient.

When experiments are done at a series of successively higher temperatures, the results may be described by¹⁶

$$n_{t_1+t_2+\dots}^2 = (4A^2C_0^2/\pi) \times (D_1^*t_1 + D_2^*t_2 + \dots) \quad (2)$$

At each temperature, a value of D^* (i.e., D_1^* , D_2^* , etc.) is obtained from the slope of a plot of n^2 against t . Finally, the data can be correlated through graphs of $\ln D^*$ against $1/T$, where one examines the possible applicability of the common Arrhenius expression

$$D^* = D_0 e^{-Q/RT} \quad (3)$$

Data for Specimen 1 are plotted in Fig. 1. The dashed line represents Eq. (3) which appears to describe the data within their precision. For several other specimens, there was some evidence that the plots of $\log_{10} D^*$ against $1/T$ became curved at lower temperatures, but this need not concern us here. We will only attempt to establish average values of D_0 and Q for comparison with other work.

Absolute values of D^* for different specimens are compared in Table I. The numerical results in the last column are based upon $A =$ (total surface area of the crystal). There are alternative

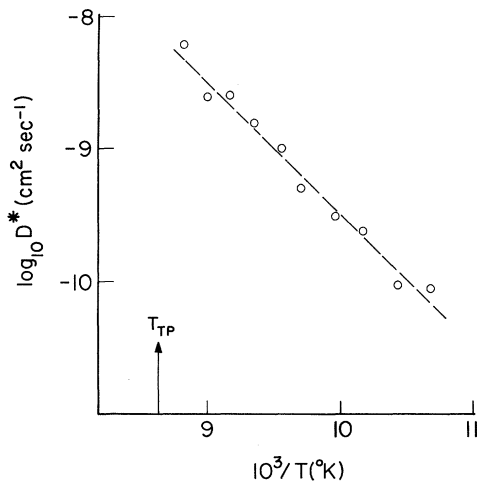


FIG. 1. ^{85}Kr diffusion in Specimen 1 as a function of temperature.

assumptions that can be made (e.g., A = top surface area = const), but the total surface area gives the minimum average deviation from the mean value of D^* for the pure specimens. Since the specimens could not be examined *in situ*, their sizes were purposely varied in an attempt to establish the proper area to be taken. The data for Specimen 3 should be given less weight because the specimen was so small.

Whatever assumption is made about the exchange area, D^* for Specimen 4 (Kr + 0.4% O_2) is lower than that for the others by a large factor. This suggests that some types of impurities may influence the concentration of point defects in the rare-gas solids. However, since an impurity such as O_2 is volatile, a full thermodynamic investigation of the system has to precede a detailed study of the dependence of diffusion upon impurity concentration. This point needs to be kept in mind in connection with the interpretation of measurements of self-diffusion in solid Xe by NMR techniques.¹⁷ About 1% of O_2 was added to

Table I. Values of D^* for different specimens at $10^3/T$ ($^\circ\text{K}$) = 9.

Specimen	Weight (g)	Total surface area (cm^2)	$10^9 D^*$ ($\text{cm}^2 \text{sec}^{-1}$)
1	6.06	9.5	3.2
2	9.70	12.2	2.6
3	1.28	5.5	1.3
4 ^a	2.50	6.9	0.5
5	3.18	7.4	2.3
6	7.27	10.4	2.2

^aKr + 0.4% O_2 .

Table II. Arrhenius parameters for self-diffusion in solid Kr.

Source	D_0 ($\text{cm}^2 \text{sec}^{-1}$)	Q (cal mole $^{-1}$)
(1) Average of present experiments	3_{-2}^{+4}	4800 ± 200
(2) Estimated through principle of corresponding states		
Experiment		
Ar ^a	~ 3.5	5300 ± 300
Ar ^b	$0.2_{-0.1}^{+0.3}$	5000 ± 200
Xe ^c	$7.1_{-0.2}^{+0.4}$	5300 ± 40
Calculated		
Ar ^d	...	5250

^aA. Bernè, G. Boato, and M. De Paz, Nuovo Cimento **46B**, 182 (1966) (tracer).

^bE. H. C. Parker, H. R. Glyde, and B. L. Smith, Phys. Rev. (to be published) (tracer).

^cYen and Norberg, Ref. 17 (NMR).

^dH. R. Glyde (unpublished).

the specimens in those experiments to enhance the resonance signals.

The average values of D_0 and Q from the experiments on pure crystals are given in Table II and compared with values obtained through the principle of corresponding states. No distinction is made between tracer diffusion and self-diffusion. The correlation factor that connects them¹⁸ probably has a numerical value that is not far from unity. Obviously the general measure of agreement between the experimental results and the estimates obtained via corresponding states is satisfactory within the limits indicated. Similar agreement has been found¹⁹ for self-diffusion in rare-gas liquids.

The value of D_0 lies within the range 0.1-10 $\text{cm}^2 \text{sec}^{-1}$ which seems generally acceptable for diffusion via intrinsic point defects.²⁰ The apparent activation energy of 4800 cal mole $^{-1}$ is consistent with that for a single-vacancy mechanism of diffusion. Divacancy and interstitial mechanisms would be expected to involve larger activation energies.^{12,14} If the diffusion occurs via single vacancies, the concentration of which is controlled thermally, Q will be the sum of the energies of formation (E_v) and migration (E_m). Losee and Simmons⁶ give $E_v = 1780 \pm 200$ cal mole $^{-1}$ from which we then obtain $E_m = 3020 \pm 400$ cal mole $^{-1}$. The ratio E_v/E_m is therefore ~ 0.59 . This is somewhat smaller than the value of unity proposed²² for vacancy diffusion in close-packed structures.

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PHOTOMAGNETIC ANNEAL PROPERTIES OF SILICON-DOPED YTTRIUM IRON GARNET

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Torque measurements have been made at 4.2°K on crystals of silicon-doped yttrium iron garnet which were irradiated with infrared light. The radiation caused large photomagnetic anneal effects which were found to depend on the plane of polarization of the light.

The effect of infrared radiation on the magnetic properties of silicon-doped yttrium iron garnet has been reported by Teale and Temple,¹ and Enz and van der Heide.² Measurements of ferrimagnetic resonance, initial permeability, and hysteresis loop shape were made. The large effects that they observed were termed photomagnetic anneal and interpreted as a light-induced redistribution of Fe²⁺ ions in the crystals. From torque curves on single crystals we have directly measured the induced anisotropy in these samples and confirmed that it can be altered considerably by photon irradiation. Changes in anisotropy up to 100×10^3 erg/cm⁻³ were observed in a sample of nominal composition Y₃Si_{0.3}Fe_{4.4}³⁺Fe_{0.3}²⁺O₁₂.

The experimental arrangement is shown in Fig

1. The sample, a sphere about 1.5 mm diam, was mounted in a conventional torque magnetometer³ such that the applied magnetic field could be rotated in a (110) plane. Infrared radiation from a 2.5-V, $\frac{1}{2}$ -W tungsten lamp inside the cryostat was polarized by a sheet of infrared Polaroid and produced approximately 10^{-3} W at the sample. The plane of polarization could be rotated through all directions in the (110) plane.

Measurements were made on crystals of nominal composition Y₃Si_{0.1}Fe_{4.9}O₁₂ and Y₃Si_{0.3}Fe_{4.7}O₁₂. At 4.2°K rotational hysteresis and time-dependent torque curves were obtained. The mean torque curves in applied fields of 15 kG were analyzed into harmonic components $\sin 2\varphi$, $\cos 2\varphi$, $\sin 4\varphi$, $\cos 4\varphi$, etc., where φ is the angle between the ap-