

the low-temperature resistance anomalies it is possible to separate, over an extended temperature range, the spin-dependent resistivity occurring in these alloys. The temperature dependence of the spin-dependent resistivity term is experimentally found to vary with  $\log T$ , and its magnitude found to vary linearly with paramagnetic impurity concentration in the solvent magnesium. Both of these experimental findings are in agreement with recent theoretical predictions of Kondo

and yield a value of  $0.76 \times 10^{-12}$  erg for the  $s-d$  exchange integral.

#### ACKNOWLEDGMENTS

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### Isotope Effect in Self-Diffusion in Palladium

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The diffusion of  $\text{Pd}^{103}$  in single crystals of palladium has been measured over the temperature range of 1050–1500°C by the tracer-sectioning technique. The results are

$$D = 0.205_{-0.04}^{+0.05} \exp[-(63\,600 \pm 650)/RT] \text{ cm}^2/\text{sec}.$$

Four measurements of the isotope effect for diffusion of  $\text{Pd}^{103}$  and  $\text{Pd}^{112}$  in each of four single crystals of palladium have been made between 1450 and 1500°C. The measured isotope effect  $E_\beta$  as defined by the equation  $E_\beta = (1 - D_\beta/D_\alpha)/[1 - (m_\alpha/m_\beta)^{1/2}]$ , where  $D_\beta/D_\alpha$  and  $m_\alpha/m_\beta$  are the ratios of the diffusion coefficients and masses of the two isotopes  $\alpha$  and  $\beta$  was found to be  $0.8134 \pm 0.0424$ . This value is consistent only with diffusion by the vacancy mechanism, and indicates that the translational kinetic energy of the activated state in the jump direction is possessed entirely by the jumping atom as it crosses the saddle point.

#### INTRODUCTION

IT is generally agreed that diffusion in crystals takes place by a series of jumps of individual atoms from one site to another throughout the crystal. For random jumps, the diffusion coefficient  $D$  for isotropic diffusion is given by

$$D = \frac{1}{6} \Gamma r^2, \quad (1)$$

where  $\Gamma$  is the jump frequency and  $r$  is the jump distance. If the direction of a given jump depends on the direction of a previous jump, then<sup>1-3</sup>

$$D = \frac{1}{6} \Gamma r^2 f, \quad (2)$$

where the correlation factor  $f$  takes into account the correlation between the directions of successive atom jumps. For self-diffusion,  $f$  is a geometrical factor determined only by the crystal lattice and the diffusion mechanism, and it can be calculated mathematically.<sup>3-5</sup> For impurity diffusion in an isotropic crystal,  $f$  depends on the jump frequencies of both the solute and solvent

species.<sup>2,6,7</sup> For impurity diffusion by the vacancy mechanism,  $0 < f < 1$ .

Since  $f$  depends only on the mechanism of diffusion, the crystal structure and, in the case of impurity diffusion, on the relative jump rates, much information can be obtained about diffusion in crystals if we can measure  $f$ . For either impurity diffusion or self-diffusion,  $f$  can be obtained from accurate measurements of the relative diffusion rates of two different isotopes of the same element. Schoen,<sup>8</sup> and later Tharmalingam and Lidiard,<sup>9</sup> derived the relation

$$(1 - D_\beta/D_\alpha) = (1 - \Gamma_\beta/\Gamma_\alpha) f_\beta, \quad (3)$$

where the  $D$ 's and  $\Gamma$ 's are the diffusion coefficients and jump frequencies of the two isotopes  $\alpha$  and  $\beta$  of the same chemical element. Using the relation  $\Gamma \propto m^{-1/2}$ , we have

$$\Gamma_\beta/\Gamma_\alpha = (m_\alpha/m_\beta)^{1/2}, \quad (4)$$

for a mechanism involving the motion of only one atom, and

$$\frac{\Gamma_\beta}{\Gamma_\alpha} = \left[ \frac{(n-1)m + m_\alpha}{(n-1)m + m_\beta} \right]^{1/2}, \quad (5)$$

<sup>1</sup> J. Bardeen and C. Herring, in *Atom Movements* (American Society for Metals, Cleveland, 1951), p. 87; also, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley & Sons, Inc., New York, 1952), p. 261.

<sup>2</sup> A. D. LeClaire and A. B. Lidiard, *Phil. Mag.* **1**, 518 (1956).

<sup>3</sup> K. Compaan and Y. Haven, *Trans. Faraday Soc.* **52**, 786 (1956).

<sup>4</sup> K. Compaan and Y. Haven, *Trans. Faraday Soc.* **54**, 1498 (1958).

<sup>5</sup> J. G. Mullen, *Phys. Rev.* **124**, 1723 (1961).

<sup>6</sup> J. R. Manning, *Phys. Rev.* **116**, 819 (1959).

<sup>7</sup> J. R. Manning, *Phys. Rev.* **128**, 2169 (1962).

<sup>8</sup> A. H. Schoen, *Phys. Rev. Letters* **1**, 138 (1958).

<sup>9</sup> K. Tharmalingam and A. B. Lidiard, *Phil. Mag.* **4**, 899 (1959).

for mechanisms involving the simultaneous motion of  $n$  atoms, where  $m$  is the average mass of the nontracer atoms. The strength of the isotope effect  $E_\beta$  was defined by Schoen as

$$E_\beta = \frac{1 - D_\beta/D_\alpha}{1 - (m_\alpha/m_\beta)^{1/2}}, \quad (6)$$

which gives  $E_\beta = f_\beta$  for the vacancy mechanism if  $\Gamma \propto m^{-1/2}$ .

The mass dependence of  $\Gamma$  is of considerable importance to the understanding of the basic jump mechanism. Considering the diffusion process to be the jump of a single atom over a potential barrier, and applying Eyring's<sup>10</sup> reaction rate theory, Wert<sup>11</sup> and Zener<sup>12</sup> obtain  $\Gamma \propto m^{-1/2}$ . This theory contains three restrictive assumptions: (1) A one-body process is assumed with no attention given to the saddle-point atoms; (2) the activated state is assumed to have a sufficient lifetime to allow assigning thermodynamic properties to it; and (3) the irreversibility of the diffusion process enters through some unspecified mechanism whereby an atom which crosses an energy barrier loses most of its energy before it can cross the barrier in the opposite direction.

Vineyard's<sup>13</sup> analysis, which takes into account the motion of the barrier atoms, indicates that  $\Gamma$  is proportional to  $(m^*)^{-1/2}$ , where  $m^*$  is an effective mass which lies between the mass of the diffusing atom and the mass of the lattice atoms. Using this analysis, Mullen<sup>14</sup> derived the relation

$$E_\beta = f_\beta \Delta K_\beta, \quad (7)$$

where  $\Delta K_\beta$  is the fraction of the translational kinetic energy of the activated state which is possessed by the jumping atom as it crosses the saddle point.

Prigogine and Bak<sup>15</sup> have proposed a one-body theory of diffusion that does not use assumptions (2) and (3). In this model, irreversibility arises from nonharmonic interactions between the normal vibration modes of the crystal lattice and the diffusing particle. The particle is assumed to move in a one-dimensional parabolic potential and to be annihilated when its energy reaches a critical value. This theory predicts that  $D$  is proportional to  $m^{-2}$  rather than the  $m^{-1/2}$  dependence predicted by reaction rate theory.

Rice *et al.*<sup>16-19</sup> have considered the many-body aspects of the diffusion process using a detailed dynamical

TABLE I. Previous measurements of the isotope effect.

Isotope	Solvent	$E_\beta$	Reference
Ni <sup>(stable isotopes)</sup>	Cu	0.96 $\pm$ 0.3	20
Fe <sup>55</sup> , Fe <sup>59</sup>	Ag	4.3 $\pm$ 1.0	21
Fe <sup>55</sup> , Fe <sup>59</sup>	Cu	0.742 $\pm$ 0.052	14
		0.590 $\pm$ 0.053	
Fe <sup>55</sup> , Fe <sup>59</sup>	Ag	0.757 $\pm$ 0.078	14
		0.487 $\pm$ 0.070	
Cd <sup>115m</sup> , Cd <sup>109</sup>	Ag, Cu	0.0 $\pm$ 0.1	8
Fe <sup>55</sup> , Fe <sup>59</sup>	Ti	0.025 $\pm$ 0.026	22
		0.093 $\pm$ 0.024	
Na <sup>22</sup> , Na <sup>24</sup>	NaCl	$\sim 1$	23
Li <sup>6</sup> , Li <sup>7</sup>	Si	0.94 $\pm$ 0.25	24
Li <sup>6</sup> , Li <sup>7</sup>	W	0.88 $\pm$ 0.25	25
H <sup>1</sup> , H <sup>2</sup>	Pd	0.75	26
H <sup>1</sup> , H <sup>2</sup>	Steel	0.89	27
C <sup>12</sup> , C <sup>13</sup>	Fe	1.07	28
Ne <sup>20</sup> , Ne <sup>22</sup>	Quartz	1.02 $\pm$ 0.20	29
He <sup>3</sup> , He <sup>4</sup>	Quartz	0.91	30
Na <sup>22</sup> , Na <sup>24</sup>	NaCl	0.711 $\pm$ 0.111	31

model not containing the three assumptions of the classical theory. They evaluate  $\Gamma$  in terms of the probability of a configuration in which the diffusing atom has a large amplitude of vibration directed towards the vacancy at the same time as an out of phase motion of the surrounding atoms opens up a hole through which the atom can pass. One interesting aspect of this model is its treatment of irreversibility; the energy is dissipated almost entirely upon recapture of the particle, and little energy is lost in transit across the potential barrier, thus suggesting that  $\Delta K_\beta = 1$ .

The few measurements of the effect of isotopic mass on diffusion, which are reported in the literature, are listed in Table I (Refs. 20-31). When more than one measurement was reported, the high and low values are given in the table. Except for the studies reported in Refs. 14, 22, and 31, these measurements are not sufficiently precise to permit many of the theoretical questions to be answered. The work of Refs. 14 and 22 was on impurity diffusion, which yields little information about  $\Delta K_\beta$ . The work of Ref. 31, which became available as this manuscript was being prepared, gives  $E_\beta = 0.711 \pm 0.111$  for self-diffusion in NaCl. This implies a  $\Delta K_\beta = 0.911 \pm 0.140$ , however, the value of  $f$  in their experiment might be less than the theoretical

<sup>20</sup> W. A. Johnson, Trans. AIME **166**, 144 (1946).

<sup>21</sup> D. Lazarus and B. Okkerse, Phys. Rev. **105**, 1677 (1957).

<sup>22</sup> G. B. Gibbs, D. Graham, and D. H. Tomlin, Phil. Mag. **8**, 1269 (1963).

<sup>23</sup> M. Chemla, Ann. Phys. (Paris) **1**, 959 (1956).

<sup>24</sup> E. M. Pell, Phys. Rev. **119**, 1014 (1960).

<sup>25</sup> G. M. McCracken and H. M. Love, Phys. Rev. Letters **5**, 201 (1960).

<sup>26</sup> W. Jost and A. Widmann, Z. Physik. Chem. **B45**, 285 (1940).

<sup>27</sup> R. C. Frank, W. L. Lee, and R. L. Williams, J. Appl. Phys. **29**, 898 (1958).

<sup>28</sup> A. J. Bosman, P. E. Brommer, and G. W. Rathenau, J. Phys. Radium **20**, 241 (1959).

<sup>29</sup> R. C. Frank, D. E. Swets, and R. W. Lee, J. Chem. Phys. **35**, 1451 (1961).

<sup>30</sup> W. M. Jones, J. Am. Chem. Soc. **75**, 3093 (1955).

<sup>31</sup> L. W. Barr and A. D. LeClaire, Trans. Brit. Ceram. Soc. (to be published).

<sup>10</sup> H. Eyring, J. Chem. Phys. **3**, 107 (1935).

<sup>11</sup> C. A. Wert, Phys. Rev. **79**, 601 (1950).

<sup>12</sup> C. Zener, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley & Sons, Inc., New York, 1952), p. 295.

<sup>13</sup> G. H. Vineyard, Phys. Chem. Solids **3**, 121 (1957).

<sup>14</sup> J. G. Mullen, Phys. Rev. **121**, 1649 (1961).

<sup>15</sup> I. Prigogine and T. A. Bak, J. Chem. Phys. **31**, 1368 (1959).

<sup>16</sup> S. A. Rice, Phys. Rev. **112**, 804 (1958).

<sup>17</sup> S. A. Rice and N. H. Nachtrieb, J. Chem. Phys. **31**, 139 (1959).

<sup>18</sup> A. W. Lawson, S. A. Rice, R. D. Corneliussen, and N. H. Nachtrieb, J. Chem. Phys. **32**, 447 (1960).

<sup>19</sup> S. A. Rice and H. L. Frisch, J. Chem. Phys. **32**, 1026 (1960).

value due to diffusion by vacancies associated with impurity atoms, which could raise their value of  $\Delta K_\beta$ . We see from the preceding discussion that a precise value of  $\Delta K_\beta$  is essential for an understanding of the role of the saddle-point atoms in the diffusion process, as well as a necessary constant for the determination of  $f$  from the experimental values of  $E_\beta$ . Since  $f$  may have a range of values for impurity diffusion, but it is a known constant for self-diffusion in a given crystal structure for a given diffusion mechanism,  $E_\beta$  must be determined for self-diffusion in order to determine  $\Delta K_\beta$ .

The present investigation was undertaken to determine the isotope effect, and thus the diffusion mechanism and  $\Delta K_\beta$ , for self-diffusion in an fcc metal. Palladium was chosen because it had two radioactive isotopes,  $\text{Pd}^{103}$  and  $\text{Pd}^{112}$ , widely separated in mass, which could be made with a high degree of radiochemical purity, and whose decay schemes permit easy separation of their respective activities. Further, self-diffusion in palladium, which had not been previously reported, could be measured simultaneously.

The two palladium isotopes were diffused simultaneously into the palladium crystal from a thin layer originally on the surface. The solution of the diffusion equation for the concentration of the tracer  $N$  after diffusion for a time  $t$  is given by the equation

$$N = \text{constant} \exp(-x^2/4Dt), \quad (8)$$

where  $x$  is the distance of penetration into the crystal. The relative concentration of the two isotopes as a function of penetration is given by

$$\begin{aligned} \ln(N_{103}/N_{112}) &= \text{constant} + (1 - D_{112}/D_{103})(x^2/4D_{112}t), \\ &= \text{constant} - \ln N_{112}(1 - D_{112}/D_{103}). \end{aligned} \quad (9)$$

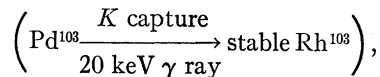
The relative isotopic diffusion rates, and hence  $E_\beta$ , may be determined without measuring the penetration distance,<sup>31</sup> and all errors due to time and temperature of the diffusion anneal cancel out.

#### EXPERIMENTAL PROCEDURE

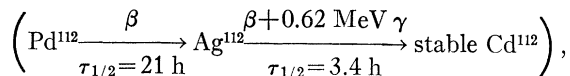
Single crystals of palladium grown from 99.999% pure material in high-purity  $\text{Al}_2\text{O}_3$  crucibles in vacuum were purchased from Metals Research Ltd. The 1.3-cm-diam crystals were spark cut into 0.6-cm-long cylinders, and the ends were spark planed flat and parallel with a Servomet spark machine. The samples were given a light etch and then annealed for 48 h in a vacuum furnace at 1200°C. After checking for monocrystallinity,  $\text{Pd}^{103}$  and  $\text{Pd}^{112}$  were electroplated on one face of the specimens. The plating bath consisted of 30 ml  $\text{H}_2\text{O}$ , 100 mg  $\text{NH}_4\text{Cl}$ , 0.6 ml  $\text{HCl}$ , and trace quantities of the Pd isotopes in the form of  $\text{PdCl}_2$ . Several atom layers of the isotopes were plated on each specimen.

The 17-d half-life  $\text{Pd}^{103}$  isotope was made by 30-MeV deuteron bombardment of rhodium by the reaction  $\text{Rh}^{103}(d,2n)\text{Pd}^{103}$ . The  $\text{Pd}^{103}$  was then chemically sepa-

rated from the rhodium target. Analysis of the gamma spectrum of the resulting carrier-free  $\text{Pd}^{103}$  solution with a 200-channel analyzer showed no radioactive impurities. Due to the simple decay scheme of  $\text{Pd}^{103}$



the detectability limit for any of the expected radioactive impurities was 0.05%. The 21-h half-life  $\text{Pd}^{112}$  isotope was made by 40-MeV  $\alpha$ -particle bombardment of uranium by the reaction  $\text{U}^{238}(\alpha, f)\text{Pd}^{112}$ . Three and one-half percent of the fission fragments from this irradiation are  $\text{Pd}^{112}$ . The  $\text{Pd}^{112}$  was then chemically separated from the uranium and the other fission fragments. The purity of the carrier free  $\text{Pd}^{112}$  solution was checked on a 200-channel analyzer and by following its decay over a period of 8 half-lives. No radioactive impurities were found. Due to the more complex decay scheme of  $\text{Pd}^{112}$ ,



with considerable background produced by the  $\beta$ 's, the detectability limit for radioactive impurities was 0.5%, while the detectability limit from the half-life determination was estimated to be 0.1%.

Two diffusion specimens were placed in an  $\text{Al}_2\text{O}_3$  cup with their active faces adjacent but separated by a flat  $\text{Al}_2\text{O}_3$  disk. The  $\text{Al}_2\text{O}_3$  cup was lined with palladium foil. A second  $\text{Al}_2\text{O}_3$  disk, a palladium foil and some palladium turnings were placed on top of the upper palladium sample. All palladium foil and turnings were of the same high purity as the samples. The  $\text{Al}_2\text{O}_3$  cup with the assembled samples was placed in a tantalum can, the can was evacuated, and a tantalum lid was electron beam welded onto the can. This procedure produced a small, evacuated container with a great deal of non-active palladium surface to minimize evaporation of the tracers. All components of the specimen assembly, except the specimens, had been previously degassed overnight at 1100°C in a vacuum furnace.

The specimens were placed in a wire-wound argon-filled tube furnace and annealed for periods of 7.5 h to 1 month, depending on the temperature. The temperature was measured with a calibrated Pt 6% Rh-Pt 30% Rh thermocouple which was in contact with the top of the 2.5-cm-long tantalum can. The thermocouple was calibrated at the melting points of Sn, Pb, Zn, Al, Ag, Cu, Ni, and Pd as well as by comparison with an NBS calibrated Pt/Pt-10% Rh thermocouple at eleven other temperatures. The emf of the Pt-6%Rh/Pt-30%Rh thermocouple at these nineteen temperatures was used to calculate the emf at 1°C increments between 231 and 1552°C by a least-squares fit of the data to a 4th-degree polynomial on a computer. The furnace temperature was maintained to within  $\pm 1^\circ\text{C}$  by an electronic controller. After the diffusion anneal, the samples were

raised to the cold part of the furnace, where they cooled to 500°C or less in 2 min. Time corrections for heating and cooling were calculated from the continuous record of the sample temperature.

The diffused specimens were mounted on a precision lathe, reduced in diameter to eliminate edge effects, and sectioned. Fifteen sections were taken from each sample; the total thickness removed ranged from 0.02 to 0.04 cm. The chips from each section were collected and weighed on a Mettler microbalance. The sum of the weights of the sections was within 0.1–0.5% of the difference in weight of the sample before and after sectioning. The thickness of each section was determined from the diameter and density of the specimen, and the weight of the section, and was corrected for thermal expansion, using the data of Holborn and Day.<sup>32</sup>

The sections were dissolved in a 50–50 HNO<sub>3</sub>–HCl mixture and transferred to polyethylene counting vials. The counting vials were checked for reproducibility by putting the same amount by weight of a Pd<sup>103</sup> solution in each of 30 randomly selected vials. The counts from the vials reproduced to within the counting statistics of 0.1%. To equalize the absorption of the 20-keV  $\gamma$  rays by the palladium ions to within 0.05%, nonactive palladium carrier was added to the dissolved sections so that each sample had the same concentration of palladium ions. The counting vials were filled with the same volume of liquid to within 50  $\mu$ l. This gave a reproducible geometry such that the counts would be the same within 0.05%.

The counting was started 34 h after the end of the diffusion anneal. This reduced the amount of Ag<sup>112</sup> which diffused as Ag by a factor of 10<sup>3</sup> and allowed the Pd<sup>112</sup>–Ag<sup>112</sup> equilibrium to be established to within 0.1%. The 0.62-MeV  $\gamma$  ray from the Ag<sup>112</sup> decay was then counted to determine the Pd<sup>112</sup> concentration. At least 2 weeks were allowed to pass before counting the Pd<sup>103</sup> activity. This permitted the Pd<sup>112</sup> and Ag<sup>112</sup> to decay by a factor of 10<sup>5</sup>, thus reducing the background in the Pd<sup>103</sup> counting range, which results from the  $\beta$ 's of Pd<sup>112</sup> and Ag<sup>112</sup>. In this manner, the isotopes were counted separately, with the background in the Pd<sup>112</sup> energy range due to the presence of Pd<sup>103</sup> being less than 0.01% of the Pd<sup>112</sup> activity and vice versa.

Prior to counting each isotope, a gamma spectrum was taken on the 200-channel analyzer from both the first and last sections to check for differences in radioactive impurity contents caused by diffusion. There was no observable difference in the spectra within the previously mentioned limits.

The samples were counted in a standard 2×2-in.-NaI(Tl) well-type scintillation crystal. The counting vials fit snugly into the well which permitted the interchanging of samples in a reproducible manner. The crystal and photomultiplier tube were surrounded by a 15-cm-thick steel shield to reduce background as well

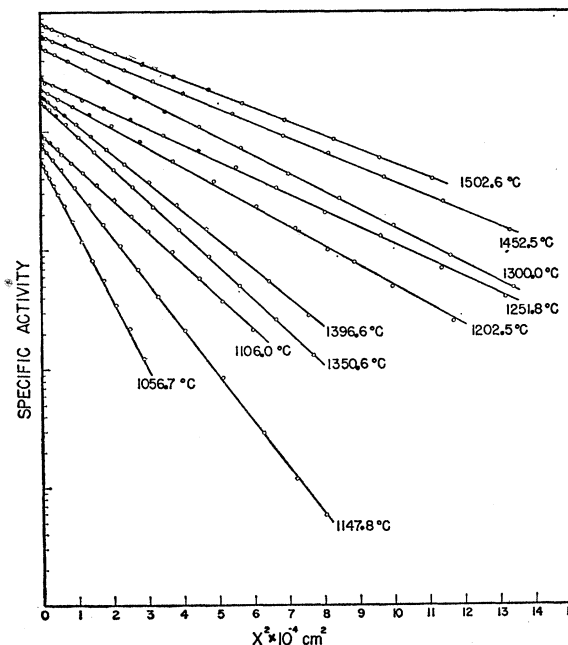


FIG. 1. Penetration curves for diffusion of Pd<sup>103</sup> in palladium.

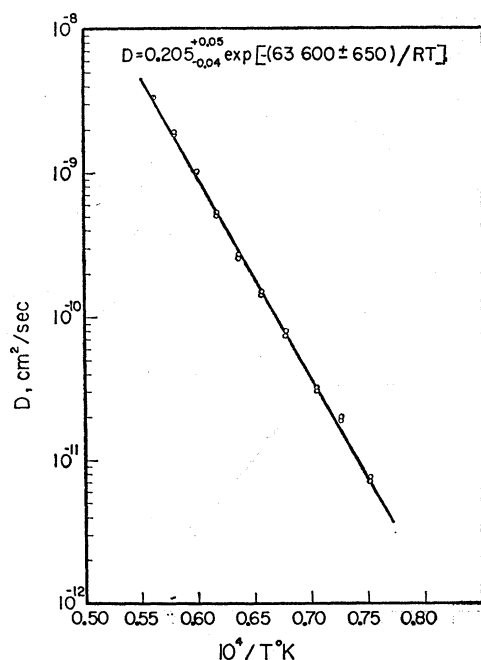
as magnetic field effects on the photomultiplier. A fast, stable, commercial single-channel analyzer, scaler, and timer were used with a highly stable high-voltage supply. The combined dead time of the scaler, analyzer, and crystal was found to be  $2.64 \pm 0.08$   $\mu$ sec. This small dead time permitted the use of very active samples, thus reducing the time over which the counter had to be stable, as well as the decay and background corrections. The high-voltage supply was found to drift no more than  $\pm 25$  mV in 1000 V over 48 h.

Each section was counted twice for each isotope, thus obtaining four independent  $\log N_{103}/N_{112}$  versus  $x^2/4Dt$  curves for each sample. The time between the first and second count for a given isotope in a given section was at least 24 h. The sections were counted in random order with the first section counted before and after every other section in order to correct for any long term drifts in the counter. A minimum of 300 000 counts above background were collected for each isotope in each section, giving a statistical uncertainty of 0.18%.

The raw counting data were corrected for the counter dead time, background, and the decay of the isotope during counting to better than 0.1%. The half-lives were found to be  $388.27 \pm 0.98$  h for Pd<sup>103</sup> and  $21.07 \pm 0.038$  h for Pd<sup>112</sup>.

Diffusion coefficients were calculated on a computer by a least-squares fit of the data to Eq. (8). The error in the diffusion coefficients due to sectioning and counting is estimated to be  $\pm 2\%$ . The error in the temperature measurements, as estimated from the calibration of many thermocouples by the above technique, ranges from 1°C at 1050°C to 2°C at 1500°C, which leads to a total uncertainty in  $D(T)$  of approximately  $\pm 4\%$ . The

<sup>32</sup> L. Holborn and A. L. Day, Ann. Physik 4, 104 (1901).

FIG. 2. Temperature dependence of  $\text{Pd}^{103}$  diffusion in palladium.

diffusion parameters  $D_0$  and  $Q$  and their errors were determined by a least squares fit of the data to the Arrhenius relation,  $D = D_0 \exp(-Q/RT)$ .

The values of  $E_{112}$  and their errors were determined by a least squares fit of the data to Eq. (9). The most serious error in the determination of  $E_{112}$  was the statistical error due to the fact that only a limited number of counts could be taken for any given specimen. This limit was imposed by the half-life of  $\text{Pd}^{112}$ , which limited the counting time, and the counter dead time, which limited the counting rate. A more accurate

determination of the half-life or of the dead time could increase the total number of collected counts, and hence improve the counting statistics, but then the stability of the photomultiplier tube would become the limiting error, so the accuracy of  $E_{112}$  would not be increased greatly. The sources and magnitudes of the systematic errors will be discussed later.

### EXPERIMENTAL RESULTS

Two measurements of  $D_{103}$  were made at each of ten different temperatures. Penetration plots for one of the two samples at each temperature are shown in Fig. 1. Temperatures and times of the diffusion anneals and the diffusion coefficients are given in Table II. An Arrhenius plot of the data may be seen in Fig. 2. The temperature dependence of  $D_{103}$  is represented by

$$D = 0.205_{-0.04}^{+0.05} \exp[-(63,600 \pm 650)/RT] \text{ cm}^2/\text{sec},$$

where  $R$  is the gas constant,  $T$  is the temperature in  $^\circ\text{K}$ , and the errors are standard errors from the least-squares treatment of the data.

The isotope effect was measured in the four crystals diffused at the top two temperatures. An attempt to determine the isotope effect at the third highest temperature failed due to a mishap in the chemical separation of the  $\text{Pd}^{112}$ . Ninety-five percent of the activity was lost, leaving too little activity for the required counting statistics. Diffusion times at lower temperatures were too long to permit the use of the 21-h half-life  $\text{Pd}^{112}$  isotope.

The eight plots of  $\log(N_{103}/N_{112})$  versus  $x^2/4D_{112}t$  for diffusion in the two palladium crystals at  $1452.5^\circ\text{C}$  are

TABLE II. Diffusion of  $\text{Pd}^{103}$  in palladium.

Temperature ( $^\circ\text{C}$ )	Time (sec)	$D_{103}$ ( $\text{cm}^2/\text{sec}$ )
1056.7	$2.653 \times 10^6$	$7.19 \times 10^{-12}$
1056.7	$2.653 \times 10^6$	$7.50 \times 10^{-12}$
1106.0	$1.975 \times 10^6$	$1.92 \times 10^{-11}$
1106.0	$1.975 \times 10^6$	$2.01 \times 10^{-11}$
1147.8	$8.729 \times 10^5$	$3.08 \times 10^{-11}$
1147.8	$8.729 \times 10^5$	$3.21 \times 10^{-11}$
1202.5	$8.634 \times 10^5$	$7.48 \times 10^{-11}$
1202.5	$8.634 \times 10^5$	$8.08 \times 10^{-11}$
1251.8	$5.166 \times 10^5$	$1.45 \times 10^{-10}$
1251.8	$5.166 \times 10^5$	$1.50 \times 10^{-10}$
1300.0	$2.646 \times 10^5$	$2.62 \times 10^{-10}$
1300.0	$2.646 \times 10^5$	$2.69 \times 10^{-10}$
1350.6	$7.440 \times 10^4$	$5.08 \times 10^{-10}$
1350.6	$7.440 \times 10^4$	$5.27 \times 10^{-10}$
1396.6	$4.500 \times 10^4$	$9.84 \times 10^{-10}$
1396.6	$4.500 \times 10^4$	$1.01 \times 10^{-9}$
1452.5	$4.440 \times 10^4$	$1.83 \times 10^{-9}$
1452.5	$4.440 \times 10^4$	$1.90 \times 10^{-9}$
1502.6	$2.700 \times 10^4$	$3.32 \times 10^{-9}$
1502.6	$2.700 \times 10^4$	$3.39 \times 10^{-9}$

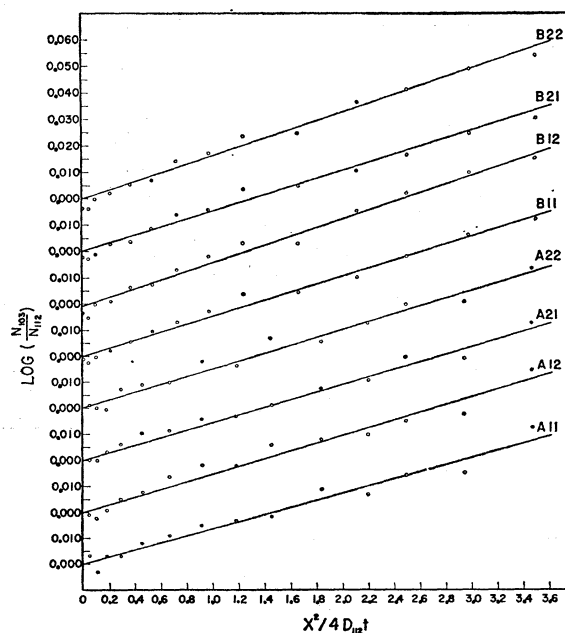
FIG. 3. Relative rates of diffusion of  $\text{Pd}^{103}$  and  $\text{Pd}^{112}$  in palladium at  $1452.5^\circ\text{C}$ .

TABLE III. Isotope effect for palladium self-diffusion.

Sample No.	Pd <sup>108</sup> count	Pd <sup>112</sup> count	$(1-D_{112}/D_{108})$	$E_{112}$	% Error	% Deviation from 0.7815
1452.5°C	1	1	0.03170±0.00195	0.7728±0.0475	6.1	-1.1
No. A	1	2	0.03369±0.00197	0.8213±0.0480	5.8	+5.1
	2	1	0.03314±0.00134	0.8079±0.0327	4.0	+3.3
	2	2	0.03431±0.00198	0.8364±0.0482	5.7	+7.0
1452.5°C	1	1	0.03298±0.00152	0.8039±0.0370	4.6	+2.8
No. B	1	2	0.03534±0.00134	0.8615±0.0327	3.8	+9.2
	2	1	0.03244±0.00152	0.7908±0.0370	4.6	+1.2
	2	2	0.03502±0.00140	0.8537±0.0341	3.9	+9.1
1502.6°C	1	1	0.03207±0.00187	0.7818±0.0455	5.8	+0.0
No. A	1	2	0.03486±0.00174	0.8498±0.0424	5.0	+8.7
	2	1	0.03217±0.00198	0.7842±0.0482	6.1	+0.3
	2	2	0.03460±0.00173	0.8435±0.0422	5.0	+7.9
1502.6°C	1	1	0.03215±0.00186	0.7838±0.0453	5.8	+0.3
No. B	1	2	0.03387±0.00217	0.8257±0.0529	6.4	+5.5
	2	1	0.03198±0.00154	0.7796±0.0375	4.8	-0.3
	2	2	0.03370±0.00194	0.8215±0.0473	5.7	+5.1
Average			0.03337±0.00174	0.8134±0.0424	±5.2	+4.0

shown in Fig. 3. *A* and *B* refer to the two crystals, respectively, the first number refers to the 1st or 2nd count of Pd<sup>108</sup> and the second number refers to the 1st or 2nd count of Pd<sup>112</sup>. A similar set of eight curves is shown in Fig. 4 for the two crystals diffused at 1502.6°C. The vertical scale is the same for all the curves in Figs. 3 and 4 and the zero position of each curve has been displaced.

The isotope effect data are listed in Table III. The first three columns identify the sample and which count of the two isotopes is being considered. Columns four and five give the values of  $(1-D_{112}/D_{108})$  and  $E_{112}$  together with their least-squares standard errors. The sixth column lists the percent standard errors and the seventh column lists the percent deviation of the measured  $E_{112}$ 's from the theoretical value of  $f_0$  (0.7815). The average values for each of the last four columns are given at the bottom of the table. It should be noted that the average deviation of the experimental values of  $E_{112}$  from the theoretical value of  $f$  (+4%) is positive and is within the average standard error in  $E_{112}$  ( $\pm 5.2\%$ ).<sup>32a</sup>

We may now discuss the three possible sources of systematic errors which could affect  $E_{112}$ . (1) Non-radioactive impurities in the palladium crystals can change the effective correlation factor. We believe that this is not a problem in this investigation because the starting material was 99.999% pure with the main possible contaminants being silver and oxygen. Both these impurities would have to be present in 100's of ppm to produce an observable effect, and this effect would be to lower  $E_{112}$  rather than the observed positive

deviation from the theoretical  $f$ . (2) Evaporation of the tracer from the sample surface could raise  $E_{112}$ , but the penetration plots of Fig. 1 show that the first point is no more than 1% below the line drawn through the points far removed from the sample surface. Since the isotopes differ only in their masses, and hence their vibration frequencies, the difference in evaporation rates should be the same as the difference in diffusion rates, 3.3%. Thus, the maximum of 1% evaporation observed in the penetration plots could only produce a 0.3% increase in  $E_{112}$ . (3) The experimental value of  $E_{112}$  could be raised if there were slow diffusing radio-

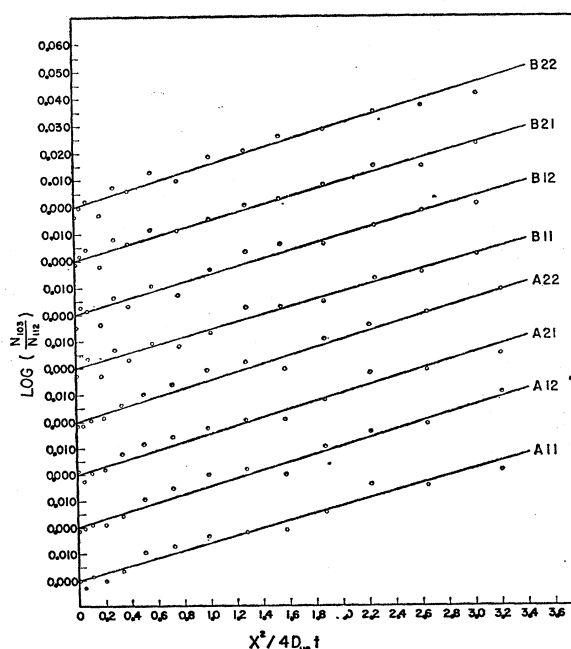


FIG. 4. Relative rates of diffusion of Pd<sup>108</sup> and Pd<sup>112</sup> in palladium at 1502.6°C.

<sup>32a</sup> Le Claire (Ref. 34) has pointed out that the experimental  $E_{112}$  must be corrected for the difference between the mass of the tracers and the average mass of the stable isotopes of palladium before comparison with the theoretical  $f_0$ . Le Claire has shown that  $E_0 = E_s(\Gamma_s/\Gamma_0)$ . Hence, from Eq. (4), we have  $E_0 = 0.8134 \times (106.4/112)^{1/2} = 0.7929$ . This is now within 1.46% of the theoretical  $f_0$ .

TABLE IV. Theoretical values of  $(1-D_{112}/D_{103})$  for self-diffusion in palladium.

Diffusion mechanism	$(1-\Gamma_{112}/\Gamma_{103})$	$f$	$(1-D_{112}/D_{103})$
Interstitial	0.04102	1.000	0.04102
Vacancy	0.04102	0.7815	0.03206
Exchange	0.02087	1.000	0.02087
Direct interstitialcy	0.02087	0.800	0.01670
4 ring	0.01050	1.000	0.01050

active impurities counted in the  $\text{Pd}^{112}$  range or fast diffusing radioactive impurities counted in the  $\text{Pd}^{103}$  range. From the previously mentioned spectra of the first and last sections of the diffusion sample, one can say that impurities counted in the  $\text{Pd}^{103}$  energy range could change  $E_{112}$  by no more than 0.4%. From the half-life determination of the  $\text{Pd}^{112}$ , we can say that there is no more than 0.1% of radioactive impurity present in the starting isotope. If the entire amount of this impurity were concentrated in the first 3 sections, it could increase the  $\text{Pd}^{112}$  count by no more than 0.5%. Further, from the analyses of the gamma spectra of the first and last sections in the  $\text{Pd}^{112}$  range, one can say there is no difference in the spectra within 0.5%, which could, however, increase  $E_{112}$  by 4%. A further indication of this error and its magnitude may be seen in Table III. For all sets of values with a common  $\text{Pd}^{103}$  count but different  $\text{Pd}^{112}$  counts, the value of  $E_{112}$  is always larger by about 5.5% using the second  $\text{Pd}^{112}$  count. This is not true for a common  $\text{Pd}^{112}$  count and different  $\text{Pd}^{103}$  counts. Between the first and second  $\text{Pd}^{112}$  counts, the  $\text{Pd}^{112}$  activity decayed by a factor of 2.5 to 3. This indicates that a slow diffusing impurity was counted in the  $\text{Pd}^{112}$  energy range and was present to 0.25% during the first count and 0.75% during the second count. Hence, this source of systematic error appears to exist, but it could not have increased the average value of  $E$  by more than 4%.

### DISCUSSION

The values of  $(1-D_{112}/D_{103})$ , calculated from Eq. (3)–(6) and the known values of  $f$  for self-diffusion for the various diffusion mechanisms, and assuming  $\Delta K_\beta=1$ , are shown in Table IV. The experimental value of  $(1-D_{112}/D_{103})$  agrees only with the vacancy mechanism. (It also agrees with the interstitial mechanism for a  $\Delta K_\beta=0.78$ . However, this is most unlikely for self-diffusion in a fcc metal.<sup>33</sup>) It may be concluded from the experimental data that  $E_{112}=f_{112}$ ,

<sup>33</sup> R. O. Simmons and R. W. Balluffi, Phys. Rev. **129**, 1533 (1963).

and  $\Delta K_\beta=1$  within the experimental error of 5.2%, so that at least 95% of the atoms move by the vacancy mechanism in self-diffusion in palladium.

The theory of Prigogine and Bak proposes  $D \propto m^{-2}$  which would give a value of  $E_{112}=3.8$ . This does not agree at all with the experimental results. Rice<sup>18</sup> has shown that the collective motion of the shell atoms will reduce the isotope effect predicted by this model, although this reduction is not expected to account for the large discrepancy between this theory and the experimental results.

The observed value of  $\Delta K_\beta$  may be explained by the Vineyard theory.<sup>34</sup> In the Vineyard formulation the only mass-dependent term is the frequency  $\nu'$ , which is the imaginary frequency of the normal saddle-point mode. Excitation of this mode leads to decomposition of the saddle-point configuration.  $\Delta K_\beta$  is the fraction of kinetic energy that resides in the migrating atom in this mode. For  $\Delta K_\beta$  to be less than one, the saddle-point atoms must move in the same direction as the jumping atom. In the close-packed fcc lattice, such motion of the saddle-point atoms is quite restricted, thus giving  $\Delta K_\beta=1$ . In the Vineyard notation this corresponds to the jumping atom moving directly across the saddle point along the normal to the hypersurface  $S$ , thus making the effective mass  $m^*$  equal to the mass of the jumping atom.

The theory of Rice *et al.* suggests that  $\Delta K_\beta$  should be one. However, the effect of the cooperative motion of the saddle-point atoms and the jumping atom on  $E_\beta$  is not clear. It would seem from the Vineyard theory that, if this cooperative motion of the saddle-point atoms is in a direction perpendicular to the jump direction, the Rice theory is also in agreement with the experimental results.

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<sup>34</sup> A. D. LeClaire (private communication).