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SELF DIFFUSION IN THORIUM

BY

C. J. MEECHAN

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20 PAGES
PHYSICS

SELF DIFFUSION IN THORIUM

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A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT AT-11-1-GEN-8
ISSUED: DECEMBER 1, 1956

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ACKNOWLEDGMENT

The author is grateful for the excellent assistance of H. Neely during the course of this work.

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ABSTRACT

The self-diffusion coefficients and activation energies for thorium have been determined from sintering data for both the face-centered-cubic and body-centered-cubic phases. The activation energies obtained are 3.6 ± 0.3 ev for the fcc phase and 4.3 ± 0.3 ev for the bcc phase. In the temperature range 1100 °C to 1550 °C, the diffusion coefficient varies from 2×10^{-10} cm^2/sec to 1×10^{-7} cm^2/sec. An analysis of the data indicates that a vacancy mechanism of volume diffusion is operative in both the fcc and bcc phases.

I. INTRODUCTION

Diffusion studies on metallic systems have received much attention in the last half century with one of the primary goals being the correlation of diffusion coefficients and activation energies with other physical characteristics of metals. Although, to date, no one theory can completely describe all of the experimental data nor accurately predict corresponding results for different systems, improvements have been made in this field in recent years due to the introduction and general acceptance of characteristic lattice imperfection theories concerned especially with vacancies, interstitials and dislocations.[1] Vacancies and interstitials are of particular interest since these defects may constitute the mechanism of diffusion in many systems.

One of the correlations of diffusion parameters and other physical characteristics which has been extensively studied is the relationship between the lattice structure of the metal and the mechanism of diffusion.[2,3] One seemingly worthwhile approach to investigating this relationship is to carry out diffusion studies on a system which exists in two separate structural phases. From this standpoint, diffusion measurements on thorium should be particularly interesting, since this metal has both a face-centered-cubic (fcc) and body-centered-cubic (bcc) phase.[4] Thus it should be possible to establish, at least for this particular system, whether or not the same mechanism of diffusion is operative for the different structures, and what effect the structure has on the diffusion coefficient.

The present paper is concerned with an experimental study designed to determine the self-diffusion coefficients and activation energies for diffusion in both the fcc and bcc phases of thorium.

II. THEORY

Since radioactive isotopes of thorium suitable for diffusion studies are unavailable, it was necessary to utilize another method for the determination of these parameters in thorium. Kuczynski[5] has developed a method for determining diffusion coefficients from the rate of sintering of metals. In this treatment, Kuczynski has derived the following equation for the flow of matter during sintering, assuming a vacancy mechanism of diffusion:

$$A|(\partial\Delta C/\partial r)_{r=\rho}|\,D' = dV/dt \qquad \ldots(1)$$

In Eq. 1 (see Figs. 1 and 2) A is the surface through which the vacancies enter the system, V is the filled volume of material between the wires, $(\partial\Delta C/\partial r)_{r=\rho}$ is the vacancy concentration gradient on the surface of radius of curvature ρ, ΔC, represents increment of concentration under the neck area and D' is the coefficient of vacancy diffusion. Kuczynski has derived the following relationships, concerning the quantities involved in Eq. 1, for such a system:

$$D'C_o = D \qquad \ldots(2)$$

$$(\partial\Delta C/\partial r)_{r=\rho} = -\delta^3\gamma C_o/kT\rho^2 \qquad \ldots(3)$$

In Equations 2 and 3, D is the coefficient of atomic diffusion, C_o is the equilibrium concentration of vacancies, δ is the interatomic distance, γ is the surface energy of the metal, k is the Boltzmann constant and T is the absolute temperature. From the above equations, and geometrical considerations, one obtains after integration

$$D = R(kT/\delta^3\gamma t)\,f(y) \qquad \ldots(4)$$

where R is a numerical constant and $y = x/a$ is the ratio of the width of the sintered interface to the wire diameter. Hence, from the known physical constants, the time-temperature history of the specimen, and the measured width of the sintered interface, and knowing R and f(y), one can determine the temperature dependence of D, the activation energy, Q, and D_o, from Eq. 4 and

$$D = D_o e^{-Q/kT} \qquad \ldots(5)$$

For the particular geometry employed in the present experiment, shown in Fig. 1, the following relationships were deduced for the quantities ρ, A and V.

$$\rho = x^2/2(a-x) \qquad \ldots(6)$$

$$A = 2\rho L[\pi-2\cos^{-1}(a/a+\rho)] \qquad \ldots(7)$$

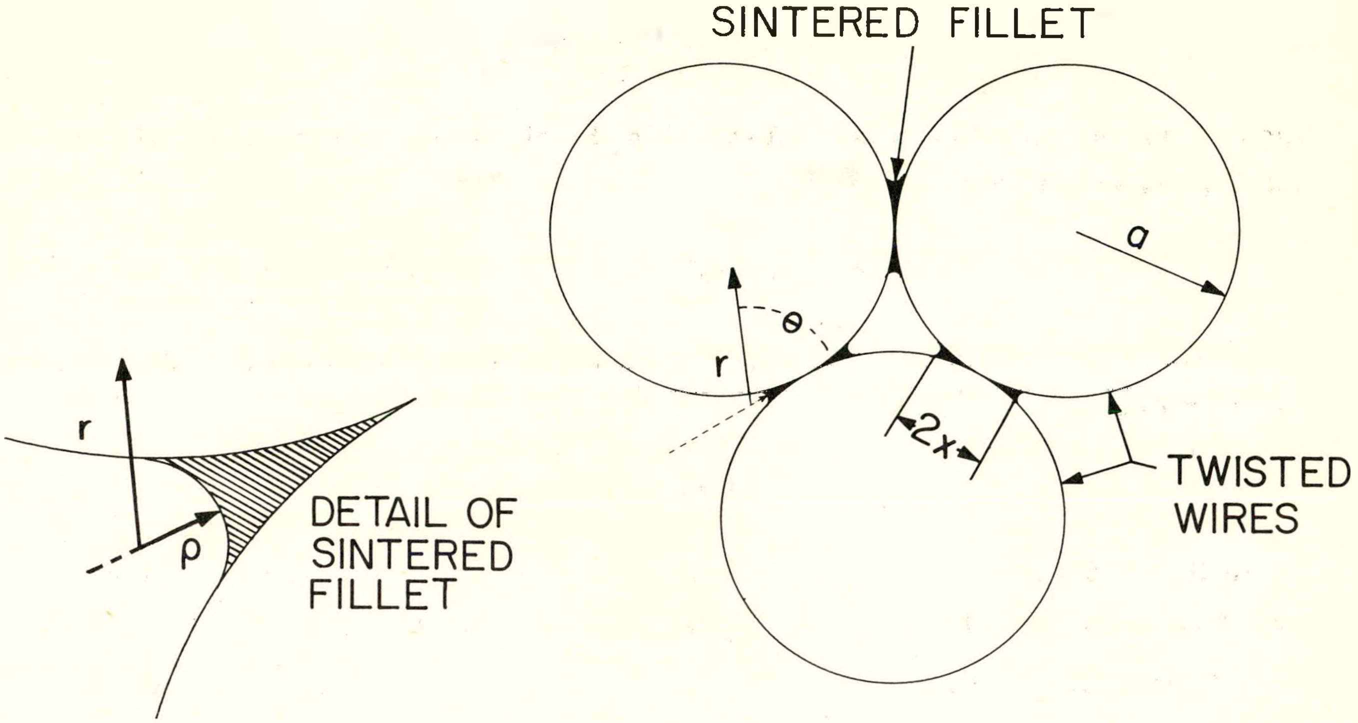

Fig. 1. Specimen Geometry

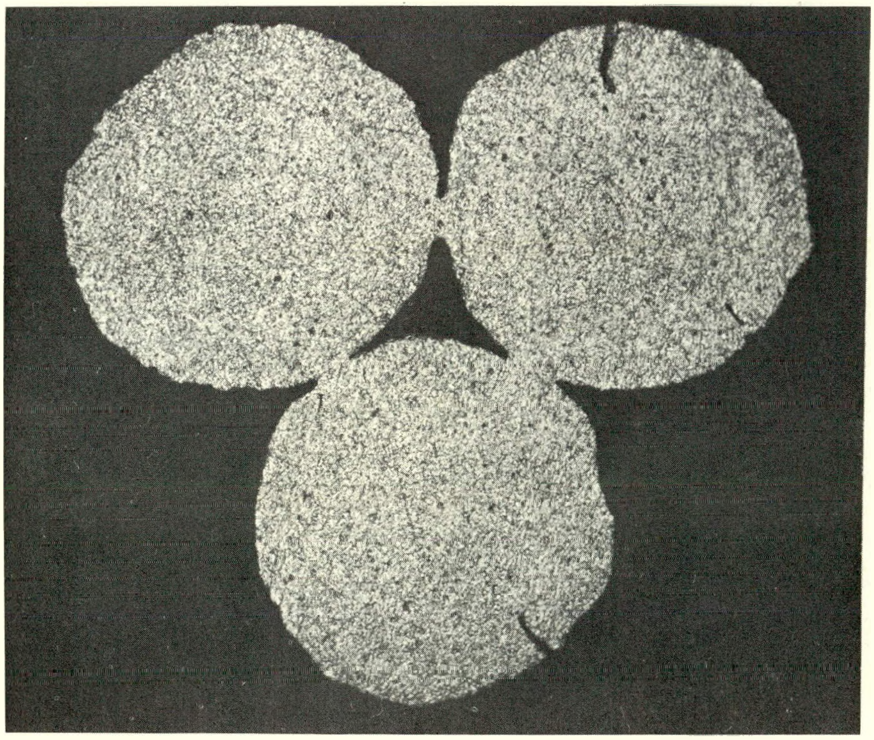

Fig. 2. Photomicrograph of Typical Specimen

$$V = 2L[a(x+\rho)-a^2\cos^{-1}(a/a+\rho)-\rho^2\sin^{-1}(a/a+\rho)] \,. \qquad \ldots(8)$$

Upon differentiating Eq. 8 and substituting the above equations, along with Eq. 3, into Eq. 1, one obtains

$$2M/a^2 = dx/dt\,[0.3183y^4 + 0.6576y^5 + 0.9981y^6 + 1.3348y^7 + 1.6684y^8 + \ldots] \qquad \ldots(9)$$

where $M \equiv \delta^3 \gamma D/kT$ and $y \equiv x/a$. Integration of Eq. 9 yields a usable form of Eq. 4, namely,

$$(2\delta^3/ka^3)(t/T)(D\gamma) = y^5 f(y) \qquad \ldots(10)$$

where $f(y) = 0.0637 + 0.1096y + 0.1426\,y^2 + 0.1668\,y^3 + \ldots\ldots$ The fourth term in $f(y)$ amounts to 4 per cent of the first term at $y = 1/4$.

Substituting the known values of some of the constants into Eq. 10, we arrive at the working equation for $D\gamma$

$$D\gamma = K(T/t\delta^3)y^5 f(y) \qquad \ldots(11)$$

where K is a numerical constant equal to 1.09×10^{-21} ergs-cm^3/°K. The reasons for leaving γ and δ in the final equation will become obvious in a later section.

In addition to determining the diffusion parameters, it is necessary to identify the mechanism responsible for sintering, e.g., surface migration, volume diffusion, viscous flow or evaporation and condensation. Herring[6] has developed the most unambiguous method with which it is possible to identify the predominant mechanism responsible for sintering under any particular set of conditions. In this treatment, simple relations are derived which govern the times required to produce geometrically similar changes by sintering at a given temperature, in two or more systems of solid specimens which are geometrically identical except for a difference in scale. For the case of sintering a cluster of wires of radius R_1, the time required to produce a given geometrical change, at temperature T, is Δt_1. For a second cluster of wires of radius R_2, the time necessary to produce a geometrically similar change at the same temperature, T, is Δt_2. The relationship between Δt_1 and Δt_2 according to Herring, is as follows for each mechanism of sintering:

$$\Delta t_2 = \lambda \Delta t_1 \qquad \text{---Viscous Flow}$$

$\Delta t_2 = \lambda^2 \Delta t_1$ ---Evaporation and Condensation

$\Delta t_2 = \lambda^3 \Delta t_1$ ---Volume Diffusion

$\Delta t_2 = \lambda^4 \Delta t_1$ ---Surface Migration

In these equations λ is the ratio of the radii of the wires (R_2/R_1). Thus one should be able to use this criterion to determine which mechanism of sintering is to be ascribed to the diffusion constants obtained from the Kuczynski method of diffusion measurements.

III. EXPERIMENTAL PROCEDURE

The two greatest difficulties encountered in carrying out such an experiment on thorium are the extremely high oxidation rate, even at relatively low pressures and temperatures, and the inability to fabricate uniform wires since it is practically impossible to pull thorium through dies without a sheathing. Therefore, the thorium wires were sheathed in copper tubes before drawing through dies and subsequently the copper was etched off in dilute nitric acid, which does not attack thorium rapidly. However, the wire uniformity was still not all that was desired and therefore many measurements of the sintered interface had to be made to statistically balance out the nonuniformities. This will be further discussed below.

Oxidation and other contamination of the specimens was minimized by performing all heat treatments in a vacuum furnace which operated under liquid nitrogen (see Fig. 3). The specimen was heated electrically and was the only component in the furnace arrangement which was heated, the walls of the furnace being maintained at liquid nitrogen temperature. In this arrangement all heat treatments were carried out at pressures less than 6×10^{-6} mm Hg. At pressures of 10^{-5} mm Hg or higher, it was found that the specimen became contaminated to the extent that, after heat treatments above 800°C, a gray film was observable. The specimens treated similarly below 6×10^{-6} mm Hg have the bright, shiny appearance of platinum. When the thorium wires were annealed in the vicinity of 1200°C for about one hour at pressures in this vicinity, it was found that they were extremely ductile and, in this respect, very similar to copper. The room

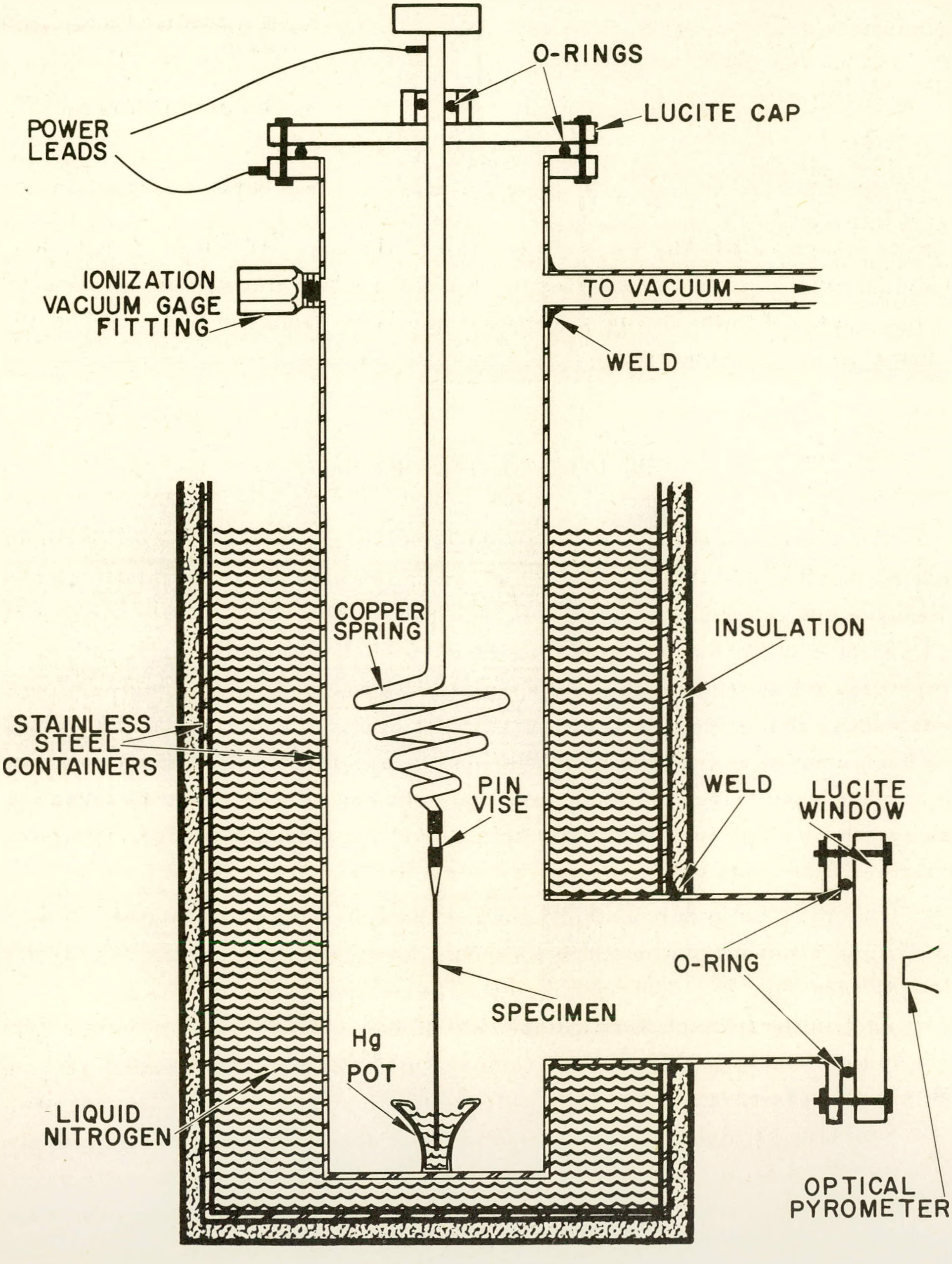

Fig. 3. Vacuum Furnace

temperature (20°C) electrical resistivity of a specimen treated in this manner is 12 μohm-cm. Because of the high ductility and low resistivity, it is believed that no significant impurities were introduced into the specimens by the heat treatment. A typical purity for iodide-processed thorium is about 99.9 per cent.

The mercury capsule at the bottom of the furnace served as one of the electrical contacts to the specimen (Fig. 3). This scheme allowed one to insert and remove the specimen without distorting or cold working the soft wires. When the furnace wall was cooled with liquid nitrogen during a heat treatment, the mercury froze around the specimen and made the electrical contact and, at the same time, held the bottom of the wire firmly so that the slack in the wire could be taken up by adjusting the rod and spring at the top.

The specimens for the diffusion study were clusters of three iodide-processed thorium wires, each 0.0196 inch in diameter, which were twisted together uniformly at 4 turns per inch under constant tension. This type of geometry produced three sintered interfaces per cross sectional cut while, at the same time, the size of the specimen was sufficiently small so that the power needed to heat the specimen in the furnace could be easily obtained.

After the wire cluster was twisted, the specimen was inserted into the furnace and sintered for various times at temperatures between 1100°C and 1550°C. Temperatures were measured with an optical pyrometer mounted next to a lucite window as shown in Fig. 3. The maximum temperature uncertainty (relative) was approximately ± 5 °C. The schedules for these treatments are tabulated in Table I. After the heat treatment, a 1-inch section was cut out of the wire cluster and mounted in plastic. The sintered section from which the measurements of the interface were taken was about 1/8 inch long. The plastic capsule containing the specimen was sectioned, polished, and electrolytically etched in a 5 to 1 volumetric solution of phosphoric and nitric acid. A typical specimen is shown in Fig. 2. The grain size in these wires was of the order of the diameter of the wires.

The width of the sintered interfaces was measured with a microscope equipped with a filar eyepiece. The specimen was repeatedly polished and etched and about 40 to 50 further measurements were made on each specimen throughout the 1/8-inch length of the cluster. These readings were then plotted on a distribution curve and an average of the readings under the portion of the curve bounded by the half width was taken as the final value. These data are included in Table I.

The measurements of the interface were substituted (along with the corresponding values of t and T) into Eq. 11 and values of Dγ were computed. In order to plot the temperature dependence of D one needs to know the surface energy, γ, for thorium. The surface tension, which should be nearly the same magnitude as γ, was measured using the sessile drop method on both copper, whose surface energy had been previously measured using different methods, and thorium. With this type of measurement, the surface tension is obtained from dimensional measurements of the surface of the drop which are determined by the forces of surface tension and gravity. It was found that the method employed here yielded values of about 20 per cent lower than those previously reported for copper. This was probably due to the fact that the measurements of the drop were made in the solid state, where the geometry of the specimen is not necessarily similar to that of the liquid state because of non-uniform cooling of the drop. The measured value for thorium was about 1600 dynes/cm; because of the above discrepancy, it is believed that a value of γ for thorium of about 2000 dynes/cm is quite reasonable, and this was the value used in the computation of D. The error in the value of γ used will have no effect on the determination of the activation energy and most probably is sufficiently small so as not to appreciably change the magnitude of the diffusion coefficients. The temperature dependence of D is shown in Fig. 4.

Additional clusters of specimens made up of 0.0196 inch, 0.0152 inch and 0.0102 inch diameter wires were heat treated in both the fcc phase and bcc phase (the phase transformation will be discussed in more detail in the next section) to determine the mechanism of sintering by use of the Herring criterion discussed in the preceding section of this paper. The results of this investigation are recorded in Table II. The data recorded in this table were obtained from two separate specimens for each temperature and the average values are given in the table.

IV. DISCUSSION

In Fig. 4, it is seen that a discontinuity exists in the ln D vs 1/T plot in the vicinity of 1425°C. This anomaly corresponds closely with the temperature at which the fcc structure transforms to bcc.[4] It is therefore believed that the discontinuity in Fig. 4 is caused by this phase transformation. The activation energies

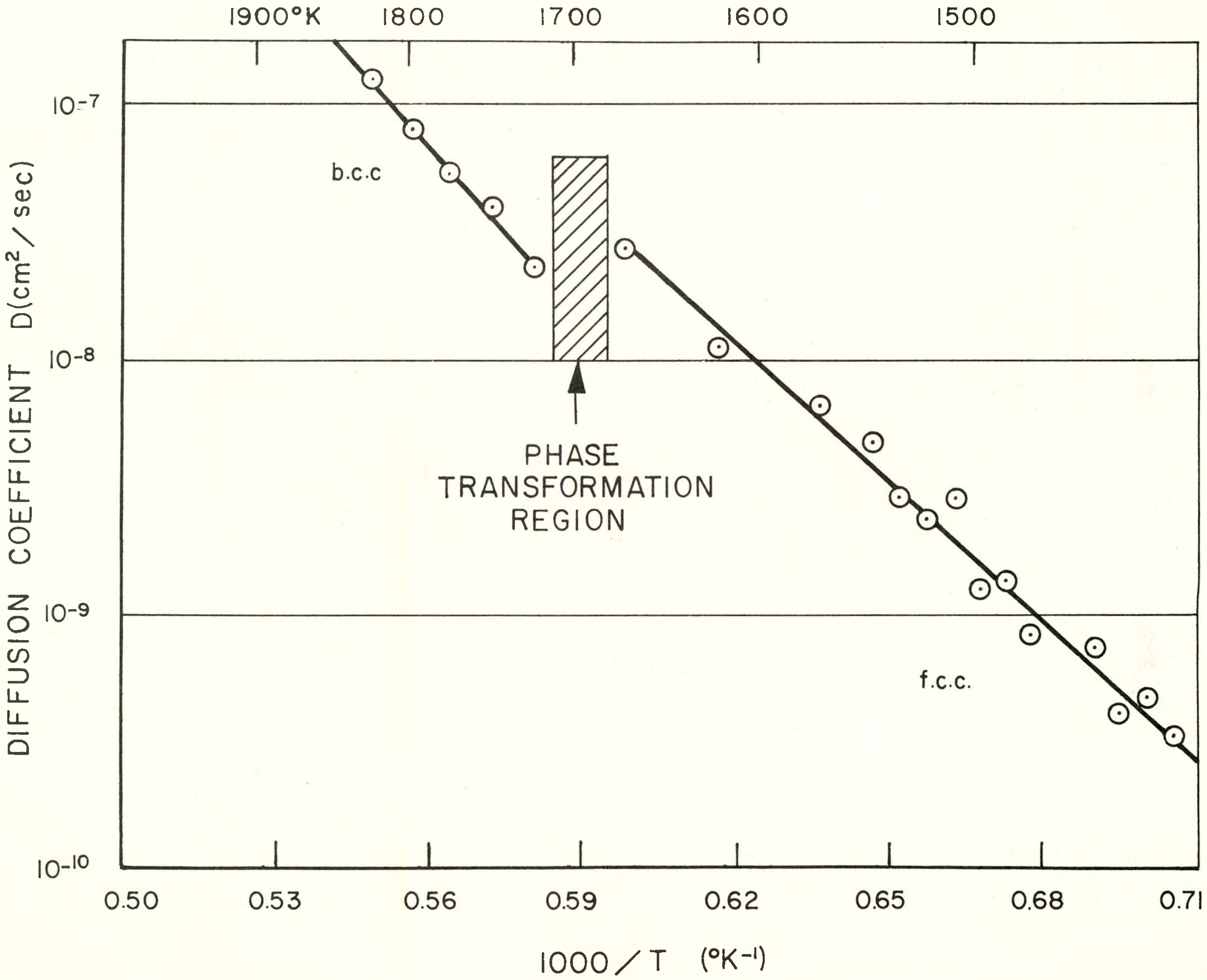

Fig. 4. Temperature Dependence of Diffusion Coefficient

for diffusion in the two phases, obtained from the slopes of the curves in Fig. 4, are 3.6 ± 0.3 ev in the low temperature phase and 4.3 ± 0.3 ev in the high temperature phase. In computing the values of D for the two phases, the same formulation was used in each case except for the value of δ which is 3.59 Å in the fcc phase and 3.56 Å in the bcc phase. This correction amounts to only about 2 per cent of the value of D.

With use of Eq. 5, the values of D_o determined were as follows: fcc phase, 100 to 5000 cm^2/sec; bcc phase, 10^4 to 10^6 cm^2/sec. Using a theory developed by Zener[7] and assuming a vacancy mechanism for diffusion, one obtains a D_o in fcc thorium of the order of 100 cm^2/sec, which is in reasonable agreement with the experimental value determined in this work. In the range 1100 to 1400°C, the values of D vary from about $2\text{x}10^{-8}$ to $2\text{x}10^{-10}$ cm^2/sec. In the high temperature phase, from 1450 to 1550°C, these values vary from about $1\text{x}10^{-7}$ to $2\text{x}10^{-8}$ cm^2/sec.

Through use of the Herring formulation for a volume diffusion mechanism, and the experimental data of Fig. 4 for the 1488°K and 1773°K temperatures, the times required to produce geometrically similar changes in smaller wires have been calculated and are given in Table II. The values of y shown in this table should be identical for each temperature. The discrepancy for the fcc phase is only 2 per cent and in the bcc phase about 3.5 per cent; therefore, these data strongly indicate that the mechanism of sintering in both phases is volume diffusion.

For this particular system, a ring mechanism of sintering in the bcc phase seems to be ruled out since it is difficult to see how the formation of the sintered fillet could even arise if such a mechanism were operative. Although it is true that volume diffusion may occur by a ring mechanism, no net mass transport takes place and therefore the sintered fillet could not be formed by such a mechanism. From energy considerations, it seems improbable that an interstitial mechanism will appreciably contribute to the sintering. These considerations, in addition to the fact that the vacancy theory of sintering satisfactorily describes the data in the bcc phase, afford the conclusion that the predominant mechanism for volume diffusion in both fcc and bcc thorium is most probably the migration of vacancies.

It should be possible to go one step further in determining the predominant mechanism for volume diffusion in bcc metals. Although the above discussion for the case of bcc thorium indicates that the mechanism is vacancy migration, one cannot state unequivocally that the ring mechanism is not contributing in any way. The possibility exists that the vacancy mechanism may be responsible for the sintered fillet, but that a ring mechanism of diffusion as well as the vacancy mechanism is operative in the crystal interior. It should be possible to add considerable insight to this question from experimental diffusion studies on bcc iron. For this case, radioactive isotopes are available with which standard diffusion measurements can be made.[8] If, in addition to this data, a sintering study is made, similar to the present investigation on thorium, the resulting activation energies and diffusion coefficients from the two experiments could be compared. If a sintered interface occurs in bcc iron, and if the activation energy and diffusion coefficients agree with those determined from the radioactive isotope diffusion study, one could reasonably conclude that the ring mechanism of diffusion is not the predominant mechanism in the bcc structure (at least for the particular case of iron). As stated in a recent review by Seeger,[9] theoretical and experimental diffusion studies on bcc structures are not nearly as complete as those on fcc structures, and therefore it is premature to decide on the most probable mechanism of diffusion in bcc metals. The above suggested experiment, which combines the results of two methods of measurement of diffusion parameters, may be quite helpful in arriving at a solution of this basic problem of diffusion in bcc structures.

Previous work (for example, see ref. 2) concerned with diffusion studies indicates that the ratio Q/T_m, where T_m is the absolute temperature of melting, is approximately a constant for all fcc metals. Recent determinations of the activation energy for self-diffusion in Co,[1] Ni,[3] and Au,[10] combined with earlier determinations on Cu,[11] Fe,[8] Pb,[12] and Ag,[13] have been used in the plot of Q vs T_m in Fig. 5. The activation energy for the fcc phase of thorium, determined in the present work, is also shown on the plot. The melting point of the bcc phase was used since it is believed that the "melting point" of the fcc phase should be nearly the same as for the bcc phase. (This is similar to the case of Fe where the bcc phase melts at 1808°K and the fcc melting point has been estimated to be 1793°K.[2] Since the data of Fig. 5 can be represented reasonably well by a straight line, and since the value for thorium in this respect agrees so well with determinations of Q in other fcc metals, additional support is obtained for the validity of the presently determined value of Q for volume self-diffusion in thorium.

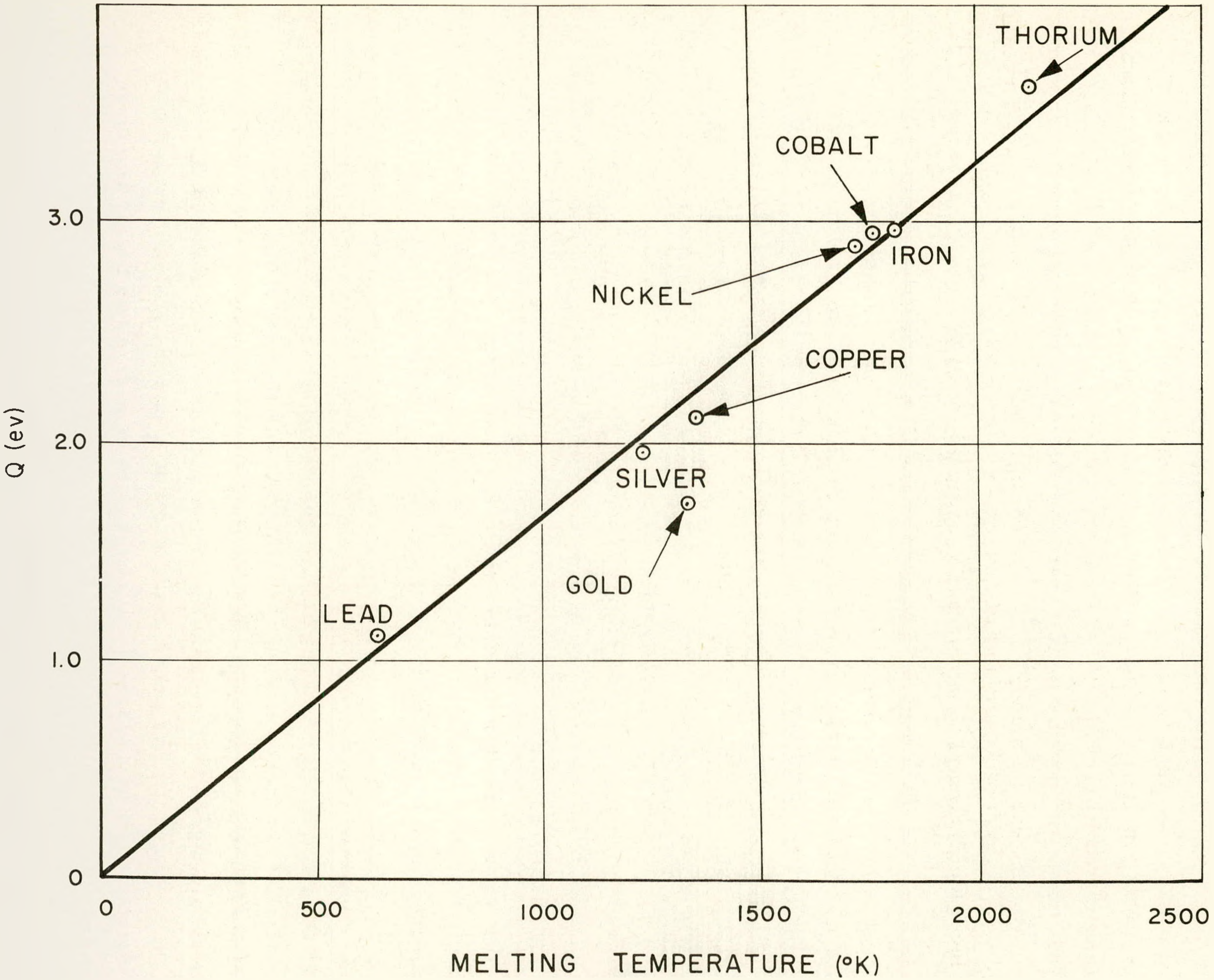

Fig. 5. Self Diffusion Activation Energy vs Absolute Melting Temperature for fcc Metals

V. CONCLUSIONS

From sintering studies on thorium, the following diffusion results have been obtained:

	fcc phase (1100°C - 1400°C)	bcc phase (1450°C 1 1550°C)
Q (ev)	3.6 ± 0.3	4.3 ± 0.3
D_o (cm^2/sec)	100 to 5000	10^4 to 10^6
D (cm^2/sec)	2×10^{-10} to 2×10^{-8}	2×10^{-8} to 1×10^{-7}

A vacancy mechanism of volume self-diffusion seems to be operative in both the fcc and bcc phases.

TABLE I

Time-Temperature History and Sintering Data for Diffusion Specimens

Temp. (°K)	Time 10^3 seconds	y 10^{-2}	D (cm^2/sec)
1418	21.60	8.96	3.33×10^{-10}
1429	18.00	9.24	4.71
1440	15.72	8.71	4.02
1450	14.40	9.61	7.34
1477	10.20	9.12	8.06
1488	10.80	10.16	1.34×10^{-9}
1499	7.20	9.24	1.24
1510	6.30	10.53	2.81
1523	5.40	9.88	2.37
1535	5.22	10.16	2.86
1548	3.60	10.35	4.60
1573	2.70	10.44	6.54
1623	2.70	11.45	1.09×10^{-8}
1673	1.80	12.47	2.63
1723	1.80	12.01	2.23
1748	1.80	13.30	3.86
1773	1.80	14.14	5.40
1798	1.80	15.06	7.63
1824	1.80	16.35	1.20×10^{-7}

TABLE II

Data for Determination of Sintering Mechanism

	Wire Diameter (cm)	Temperature (°K)	Time (min)	Interface Width, 2x (cm)	y
Face Centered Cubic Phase	0.0498	1488	180[a]	0.00506	0.102
	0.0259	1488	25[b]	0.00258	0.100
Body Centered Cubic Phase	0.0498	1773	30[a]	0.00704	0.141
	0.0386	1773	14[b]	0.00524	0.136

[a] These times were arbitrarily chosen in obtaining the data for Fig. 4.

[b] These times were calculated from the Herring formulation for a volume diffusion mechanism, using the time-temperature history of the 0.0498 cm diameter wires as standards.

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