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Isotope Effect for Diffusion of Iron in Vanadium*†

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The diffusion coefficients of iron, using Fe^{59} as the radioactive tracer, and the isotope-effect parameter, using Fe^{55} and Fe^{59} as tracers, have been measured in vanadium over a temperature range of more than 800°C by standard sectioning and counting techniques. The diffusion of Fe^{59} in vanadium exhibits the anomalous behavior of having not one but two straight lines in a plot of $\ln D$ versus $1/T$, with a change of slope occurring near 1350°C. The data have been analyzed into the sum of two exponentials: $D=2280\exp(-101\,500/RT)$ at high temperatures, and $D=0.0936\exp(-67\,600/RT)$ at low temperatures. The values of the isotope-effect parameter for the Fe^{59} and Fe^{55} isotopes are approximately constant near 0.7 at low temperatures, but decrease rapidly with increasing temperature above 1350°C. The measurements are interpreted to indicate that two mechanisms of diffusion operate in vanadium. The mechanism predominant at low temperatures is identified as motion of a single vacancy; that at high temperatures is probably motion of divacancies.

I. INTRODUCTION

STUDIES of diffusion of radiotracers have shown that for most metals the diffusion coefficient D can be expressed as a function of absolute temperature T through a simple Arrhenius relation

$$D=D_0\exp(-Q/RT), \tag{1}$$

where D_0 is the frequency factor, Q is the activation energy, and R is the gas constant. Within experimental error, D_0 and Q are temperature-independent, and a plot of $\ln D$ versus $1/T$ is linear. Measurements of the self-diffusion coefficients for most metals have given values of D_0 which are within an order of magnitude of 0.5 (cm^2/sec) and Q's which are about $36T_{\text{melting}}$ cal/mole.

Several body-centered cubic metals deviate from this so-called "normal" diffusion behavior and are classed as "anomalous" metals. Four of these anomalous metals, β-Zr, β-Ti, β-Hf, and γ-U, exhibit continuously curving Arrhenius plots (on a $\ln D$-versus-$1/T$ graph) and/or very low values of D_0 and Q.[1–4] Two others, V and Cr, have such Arrhenius plots consisting of two straight lines, showing either an abrupt change of slope or line curvature over a very narrow temperature range.[5,6] In contrast to the first group, the low-temperature values of D_0 and Q for Cr and V fall within the ranges of values found for normal metals; but the values at high temperatures are considerably higher than expected. The present work is a further study of the anomalous behavior of diffusion in V.

Explanations of the anomalous behavior observed in these metals range from impurity effects to short circuiting paths to changes in mechanism; they have been discussed extensively by LeClaire,[7] Lazarus,[8] and Kidson.[9] A plausible explanation involving a change of mechanism has been proposed recently by Peart and Askill.[10] Their view is that two competing mechanisms of diffusion occur in metals, diffusion by a single vacancy mechanism which is predominant at low temperatures and diffusion by a divacancy mechanism, predominant at high temperatures. In their interpretation, the temperature at which the divacancy contribution becomes significant is above the melting point in the normal metals and below in anomalous metals.

The present study is principally a study of the isotope effect for diffusion in vanadium. Measurements were made both above and below the break in the Arrhenius plot to determine if the anomaly observed is the result of a change in diffusion mechanism.

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[7] A. D. LeClaire, in *Diffusion in Body-Centered Cubic Metals* (American Society for Metals, Cleveland, Ohio, 1965), p. 3.

[8] David Lazarus, in *Diffusion in Body-Centered Cubic Metals* (American Society for Metals, Cleveland, Ohio, 1965), p. 155.

[9] G. V. Kidson, in *Diffusion in Body-Centered Cubic Metals* (American Society for Metals, Cleveland, Ohio, 1965), p. 329.

[10] R. F. Peart and J. Askill, Phys. Status Solidi **23**, 263 (1967).

II. THEORY

One way of differentiating between the several possible mechanisms is to use the isotope effect. This effect may be expressed analytically in terms of a parameter E_B defined as

$$E_B = \frac{1 - D_B/D_A}{1 - (m_A/m_B)^{1/2}}. \tag{2}$$

This expression applies to the case of one atom changing position in the lattice during the diffusional process. D_A and D_B are the diffusion coefficients of two isotopes of the same element with masses m_A and m_B.[11] If only one atom changes position in the lattice but others share in the motion during the jump, the isotope effect has been shown to be

$$E_B = f\Delta K, \tag{3}$$

where f is called the correlation factor and ΔK has the physical significance of being the fraction of the total translational kinetic energy possessed by the diffusing atom in the diffusion direction during the jump.[12,13] The correlation factor has different values for different mechanisms of diffusion. If ΔK is relatively insensitive to the mechanism of diffusion or varies directly with the correlation factor, a change in mechanism will produce a change in the value of the isotope effect. No way currently exists for predicting the effect of a change of mechanism on ΔK, however.

Generalization of Eq. (2) is necessary if the mechanism of diffusion involves the translation of more than one atom. In this case the masses, m_A and m_B, must be replaced by effective masses, m_A^* and m_B^*, defined as

$$\begin{aligned} m_A^* &= m_A + (n-1)m, \\ m_B^* &= m_B + (n-1)m, \end{aligned} \tag{4}$$

where n is the total number of atoms changing position and m is the average mass of the matrix atoms.[14] Clearly, a change of mechanism which alters the number of atoms changing positions will lead to a change in the value of the parameter E_B.

III. EXPERIMENTAL PROCEDURES

A. General

Values of the diffusion coefficients were determined by measuring penetration of radiotracers into bulk specimens of vanadium. Thin layers of two radioactive isotopes, Fe^{55} and Fe^{59}, were applied to the plane ends of specimens of vanadium, the specimens annealed and sectioned, and the sections counted. The boundary conditions were those of an instantaneous plane source in a semi-infinite crystal. The concentration c of one radiotracer can be given as a function of the penetration distance x as

$$c = M/(\pi Dt)^{1/2} \exp(-x^2/4Dt). \tag{5}$$

Here M is the initial concentration at the interface and t is the annealing time. Thus, the slope of a plot of $\ln c_B$ versus x^2 gives the factor $-1/4D_Bt$. The relative concentration of the two isotopes, A and B, can be shown from Eq. (5) to be

$$\ln(c_A/c_B) = \text{const} + (1 - D_B/D_A)(x^2/4D_Bt). \tag{6}$$

Thus, a plot of $\ln(c_A/c_B)$ versus $(x^2/4D_Bt)$ permits determination of $(1 - D_B/D_A)$; this number is proportional to the isotope effect, Eq. (2). Errors arising from the preparation of the specimens and the annealing time and temperature were eliminated from the determination of $(1 - D_B/D_A)$ by the simultaneous diffusion of the tracers.

The diffusion specimens were zone-refined single crystals of vanadium, prepared by Leytess Metal and Chemical Corporation. From three to seven zone passes were used by them in the zone refining. The crystals were cylindrical in shape, approximately 0.5 in. in diameter, and about 0.5 in. long. Specimens were annealed near the melting point of vanadium, before application of the tracers, to reduce the number of short circuiting paths.

The radioactive tracers were obtained as chlorides in aqueous solution. They were mixed and applied to the end faces of the vanadium specimens by one of two methods, by electroplating from a saturated solution of ammonium oxalate or by drying the aqueous solution directly onto the specimen. No difference could be seen, within experimental accuracy, between these two methods; and the second method was used for most anneals because of its simplicity.

Specimens were made up in three geometries. For anneals below 1300°C, the tracer was simply applied to the end faces of the crystal. Two other geometries were used at higher temperatures where loss of both tracer and vanadium occurs by vaporization. In one method, the tracer was sandwiched between two single crystals held together with a light pressure by wire. The two crystals sintered together during the anneal, however, and could not be separated subsequently. Alignment for sectioning could only be done visually by means of microscopic examination of the external edge of the interface between the two crystals, not a completely satisfactory technique. Another geometry was then devised to minimize evaporation and yet to allow good alignment for sectioning. In this method, a hollow cap of vanadium was placed over the plated ends of the specimen. This cap could easily be machined away after annealing leaving the end face free for alignment.

Two furnaces were used for the diffusion anneals. The anneals below 1100°C were made in a standard resistance-wound furnace. Control of this furnace was

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[12] James G. Mullen, Phys. Rev. 121, 1649 (1961).

[13] A. D. LeClaire, Phil. Mag. 14, 1271 (1966).

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approximately ±1°C. Specimens were annealed at higher temperatures in an electron beam furnace with control of about ±1.5°C below 1350°C and ±2°C above 1500°C. Temperature was controlled and monitored in both furnaces using thermocouples appropriate for the temperatures. These thermocouples were calibrated in place before and after each anneal against melting points of at least two metals which were nearest to the temperature of the anneal. Vacuum in these furnaces ranged between 10^{-6} and 10^{-5} Torr at the annealing temperature.

Specimens annealed at temperatures above 1200°C were sectioned in a lathe. With this well-known technique, consecutive slices were removed from the specimen parallel to the end face, and the chips collected, weighed, and counted. Sections of 0.0004 to 0.001 in. thickness were typical. The distance of penetration was determined from the weight of the section, the diameter of the specimen, and the density of vanadium.

The specimens other than those with the sandwiched tracer were aligned for sectioning by mounting them in a lathe and advancing a soft metal probe to the edges of the end face until electrical contact was made between the probe and the specimen. Alignment with this technique was always within 0.00002 in. at the edge of the specimen. A ring of material concentric to the specimen axis was removed from the sides of each specimen to eliminate the effects of surface diffusion down the sides of the specimen. Enough material was removed to ensure that any tracer which could have been on the sides of the specimen, and subsequently diffused inward, was removed and could not contribute to the counting rates of the sections.

Chemical sectioning was used at lower temperatures where penetration of the tracers is too small for lathe sectioning. After the side cut was made on a lathe, the side was masked off with an acid-resistant epoxy resin. The face of the specimen was then etched away in a solution of equal parts of nitric acid, acetic acid, and water. The etching solution was then dried and counted. Section thickness was measured by weighing the specimen before and after each section was taken. Sections about one micron thick were taken by this method, allowing the measurement of much smaller diffusion coefficients than could accurately be measured by lathe sectioning techniques.

B. Counting

The two iron isotopes used have quite different decay schemes. The Fe^{59} isotope, with a half-life of 45.5 days, emits a 0.46-MeV β ray and a number of γ rays including ones with energies of 1.1 and 1.3 MeV. The other isotope, Fe^{55}, decays with a 2.94-yr half-life by internal conversion and emits only a 5.9-keV γ ray. Selective counting of the two isotopes is, thus, easy in principle.

Simultaneous counting of the two tracers was performed with scintillation counting equipment using two channels. The Fe^{59} was easily counted in the presence of the Fe^{55} by measuring only the high-energy γ rays. Counting the Fe^{55} γ ray was not so easy, however, since some Fe^{59} radiation was always counted in this channel. It was always necessary, therefore, to count a pure Fe^{59} standard, measure the fraction of Fe^{59} appearing in the Fe^{55} channel, and correct the Fe^{55} counting rate by this fraction of the counts in the Fe^{59} channel.

TABLE I. A summary of the diffusion of Fe^{59} in V. Specimens used with Fe^{55} present in addition to Fe^{59} as noted.

T (°C)	$10^4/T$ (°K^{-1})	Isotopes	Geometry	D_{59} (cm^2/sec)
960	8.11	Fe^{59}	Open end	1.01×10^{-13}
				9.32×10^{-14}
1009[a]	7.80	Fe^{59}, Fe^{55}	Open end	2.90×10^{-13}
				2.88×10^{-13}
1065	7.48	Fe^{59}, Fe^{55}	Open end	9.09×10^{-13}
1210	6.74	Fe^{59}, Fe^{55}	Open end	1.24×10^{-11}
1297[a]	6.37	Fe^{59}, Fe^{55}	Open end	4.96×10^{-11}
1345[a]	6.18	Fe^{59}, Fe^{55}	End cap	1.05×10^{-10}
1415[a]	5.92	Fe^{59}, Fe^{55}	End cap	3.20×10^{-10}
1448[b]	5.81	Fe^{59}	Sandwich	5.33×10^{-10}
1448	5.81	Fe^{59}	Sandwich	5.43×10^{-10}
1505[a]	5.62	Fe^{59}, Fe^{55}	End cap	1.29×10^{-9}
1556	5.47	Fe^{59}, Fe^{55}	Sandwich	2.48×10^{-9}
1645[a]	5.21	Fe^{59}, Fe^{55}	End cap	8.73×10^{-9}
1762	4.91	Fe^{59}	Sandwich	3.35×10^{-8}
1817[a]	4.78	Fe^{59}, Fe^{55}	End cap	6.06×10^{-8}

[a] Used for isotope-effect measurements.

[b] Tracer electroplated on specimen. Tracers applied as FeCl_2 on all other specimens.

The factor $1/4D_{59}t$ and the diffusion coefficients of Fe^{59} were determined first for each specimen. Counting was performed with a NaI(Tl) crystal as the scintillation detector.

Counting of the two isotopes for determination of their relative diffusion coefficients was possible only after a considerable amount of further preparation of the sections. This was necessary because vanadium has a high mass absorption coefficient (approximately 500 cm^2/g) for the 5.9-keV γ ray emitted from the Fe^{55}. Dependable and reproducible counting of this low-energy γ ray required the removal of the iron tracers from the vanadium. This separation was accomplished by a solvent extraction method. (A number of diffusion specimens containing both Fe^{55} and Fe^{59} were ruined during initial attempts to achieve separation of the Fe tracers from the vanadium. These are noted in Table I.)

Measurement of the relative diffusion coefficients required measurement only of the relative amounts of the two tracers in each section, not of their absolute amounts, so removal of all the tracer from the vanadium was not necessary. The two iron isotopes behave the same chemically and were removed quantitatively and in equal proportions from the sections with this method. Evidence of this was seen in the subsequent counting of the two isotopes: The penetration profiles of the Fe^{59} were reproduced within ±2% mean deviation.

The measurement itself was made in the following way. Each section from the diffusion specimen was first dissolved in the nitric acid, acetic acid, and water mixture. The sections were then normalized to the same vanadium content by removal of portions of the solutions. The normalized sections were then dried and redissolved in hydrochloric acid. Isopropyl ether, which is immiscible with the aqueous solution of the section, was then added and the mixture shaken vigorously. The iron tracers are preferentially absorbed in the isopropyl ether, while only a very small proportion of the vanadium is absorbed. The aqueous solution containing most of the vanadium was then discarded and the isopropyl ether scrubbed with hydrochloric acid several times to reduce even further the amount of the vanadium present with the iron. The isopropyl ether was then evaporated, leaving the tracers in the residue. Determination of the factor $(1-D_{59}/D_{55})$ was made by counting the two tracers simultaneously in a two-channel liquid scintillation system as described by Dern and Hart.[15] The residue from the solvent extraction was dissolved in the liquid scintillator, PPO and POPOP in Bray's solution.[16] This intimate mixing of the tracers with the scintillator further reduced the absorption effects of the vanadium on the 5.9-keV γ ray.

III. EXPERIMENTAL RESULTS

Representative penetration profiles of Fe^{59} in vanadium obtained by the lathe sectioning technique are shown in Fig. 1, and by chemical sectioning in Fig. 2.

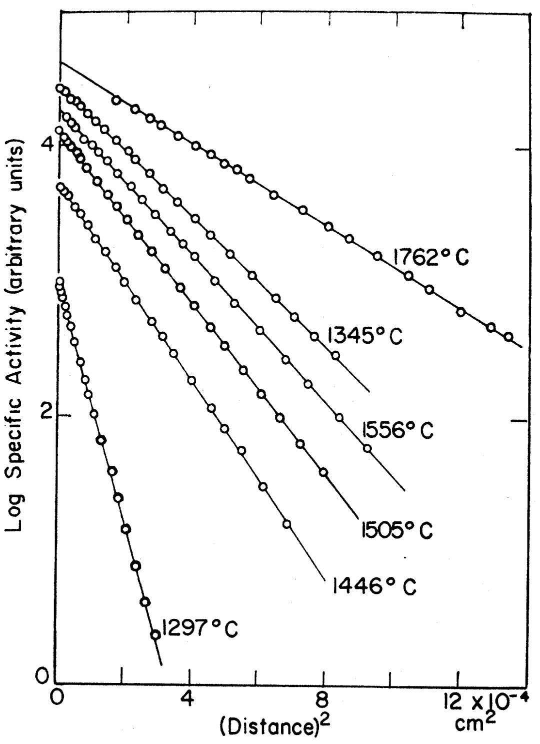

FIG. 1. Representative penetration profiles of Fe^{59} in V by lathe sectioning.

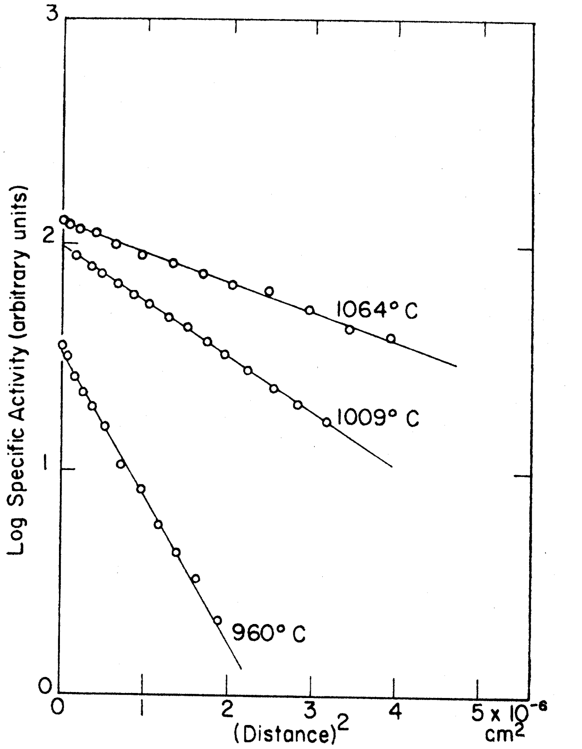

FIG. 2. Penetration profiles of Fe^{59} in V by chemical sectioning.

The profiles for lathe sectioning extend over several orders of magnitude of the counting rate and are linear on the $\log c$ versus x^2 plot. The profiles for chemical sectioning are equally linear on this plot but extend over a smaller range of the counting rate. The data for the diffusion of Fe^{59} in vanadium are summarized in Table I. The diffusional behavior of Fe^{59} in vanadium, as seen in the $\log D$ versus $1/T$ plot, Fig. 3, is similar to that of self-diffusion in vanadium with two straight lines having a change of slope near 1350°C. The two straight-line segments of this plot are described by

$$D=(274\pm15)\exp[(-92\,170\pm105)/RT]$$

at high temperatures and by

$$D=(0.373\pm0.051)\exp[(-71\,000\pm180)/RT]$$

at low temperatures. These values compare closely with the values for D_0 of 214 and 0.36 cm^2/sec and for Q of 94 140 and 73 650 cal/mole at high and low temperatures, respectively, measured for self-diffusion in vanadium by Peart.[5] Peart also measured the diffusion of Fe^{59} in vanadium between 842 and 1171°C and obtained

$$D=(0.60\pm0.15)\exp[(-70\,500\pm250)/RT],$$

which yields slightly larger diffusion coefficients than those of the present work. The discrepancy can be attributed primarily to the inclusion of some dislocation enhanced diffusion in Peart's penetration profiles for the diffusion of Fe^{59} in vanadium. A detailed inspection

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[15] R. J. Dern and W. L. Hart, J. Lab. Clin. Med. 57, 321 (1961).
[16] G. A. Bray, Ann. Biochem. 1, 23 (1960).

of Peart's penetration profiles for Fe^{59} in vanadium shows a straight-line segment through the initial sections with a small curvature showing enhanced diffusion at deeper sections. Values of the diffusion coefficient reported here do not include this enhanced diffusion and are thus lower in magnitude. Dislocation diffusion was observed to have a much more pronounced effect on the diffusion of Fe^{59} in vanadium than was seen for self-diffusion in vanadium.

The largest source of error is the inaccuracy of temperature measurement (for example, an error of ±2°C at 1500°C; an error in the diffusion coefficient of ±5%). Other errors, such as weights for the measurement of distance, and counting errors, were 1% or less. The total error in any single value of the diffusion coefficient of Fe^{59} in vanadium measured in this work is estimated to be no more than 5%.

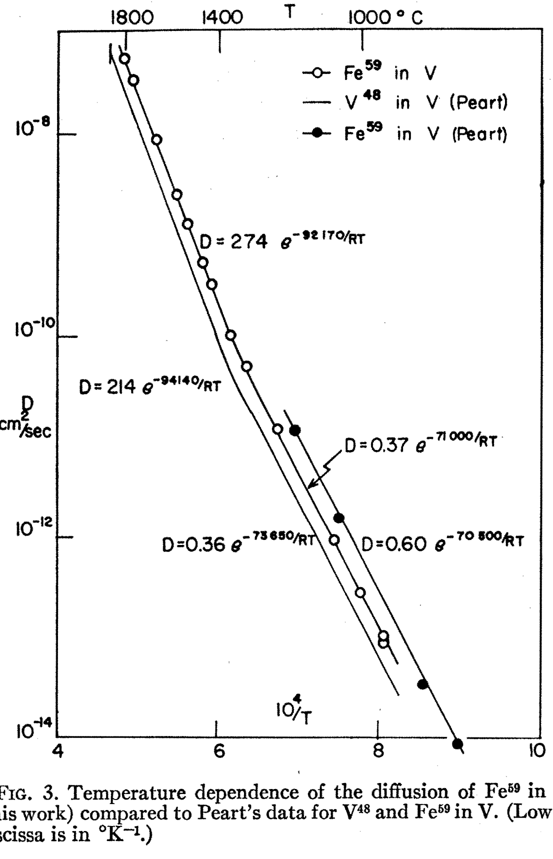

FIG. 3. Temperature dependence of the diffusion of Fe^{59} in V (this work) compared to Peart's data for V^{48} and Fe^{59} in V. (Lower abscissa is in $°K^{-1}$.)

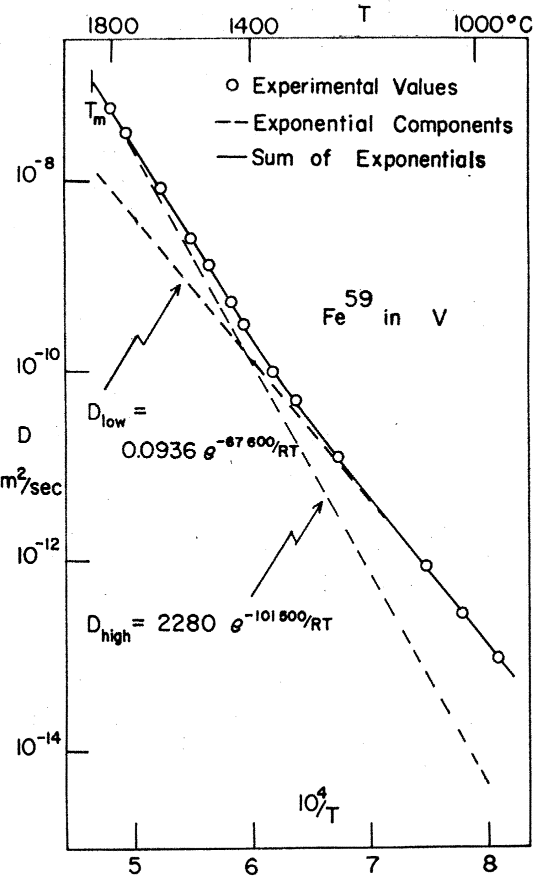

FIG. 4. Decomposition of data for diffusion of Fe^{59} in V into the sum of two exponentials. (Lower abscissa is in $°K^{-1}$.)

The measured data will be the sum of two Arrhenius equations if two mechanisms of diffusion are operative over the entire temyerature range. In order to test this possibility, the low-temperature data were extrapolated to high temperatures and subtracted from the measured values at high temperatures. The diffusion coefficients obtained in this manner, designated D_{high}, were extrapolated to low temperatures and subtracted from the measured values at low temperatures to give values of D_{low}. This process was repeated several times. The resolved data fall on two straight lines within experimental errors, Fig. 4, with

$$D_{\text{high}} = (2280 \pm 240)\exp[(101\,500 \pm 380)/RT]$$

and

$$D_{\text{low}} = (0.0936 \pm 0.0165)\exp[(-67\,600 \pm 320)/RT].$$

It should be noted that the sum of two exponentials is not two straight lines on a semilogarithmic plot, but shows curvature. The curvature in the present case is small except in the region where the two exponentials have nearly the same values because of the large differences between both the D_0 factors and the activation energies. Thus, to a good approximation, both the values for the measured values and the component exponentials can be expressed as exponentials.

A large change in the isotope-effect parameter was seen as the temperature was varied. The measured values of the isotope-effect parameter are approximately constant near 0.7 below 1350°C, but decrease rapidly above this temperature. Plots of the relative diffusion rates of diffusion of Fe^{55} and Fe^{59} in vanadium are shown in Fig. 5. The values of this parameter and the relative diffusion coefficients of Fe^{55} and Fe^{59} are given

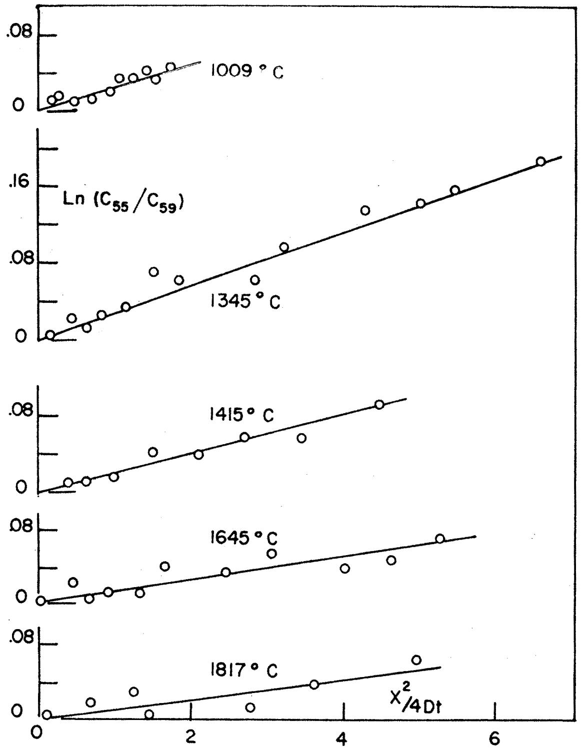

FIG. 5. Plots of the relative rates of diffusion of Fe^{55} and Fe^{59} in V.

in Table II. The temperature dependence of the isotope effect is shown in Fig. 6.

IV. DISCUSSION AND CONCLUSIONS

The data measured in this work conclusively indicate that two mechanisms of diffusion operate in vanadium. The most significant evidence is the large change in the isotope-effect parameter at high temperatures. The data over the entire temperature range measured can be analyzed as the summation of two Arrhenius equations, giving further support to a two mechanism model.

The predominant mechanism of diffusion at low temperatures is consistent with diffusion by single vacancies. The activation energy and D_0 for both Fe^{59} and self-diffusion in vanadium at low temperature agree quite closely with the empirical rules for diffusion in normal metals, which diffuse by a single vacancy mechanism, indicating qualitatively that the diffusion is by single vacancies. The measured values of the isotope-effect parameter below 1350°C give quantitative evidence for a single vacancy mechanism. The theoretical value for the correlation factor, f, for diffusion by a single vacancy in a body-centered cubic lattice is 0.72. The values of the isotope-effect parameter measured in this work, which are of a product of the correlation factor and ΔK, average about 0.69 in the low-temperature range. The value of ΔK must therefore be very close to 1.0. Measurements by Graham of the isotope-effect parameter in the self-diffusion of body-centered cubic iron give values of ΔK very close to 1.0.[17] The iron atom is approximately 7% smaller than the vanadium atom, allowing it to move through the vanadium lattice with smaller displacements of the surrounding atoms than for the case of self-diffusion in iron. The ΔK factor, therefore, would be expected to be very close to unity for the present work.

TABLE II. Measurements of the relative diffusion coefficients of Fe^{55} and Fe^{59} in V and values of the isotope-effect parameter.

Temperature (°C)	$(1-D_{59}/D_{55})$	E_B
1009	0.0235	0.681±0.047
1297	0.0240	0.695±0.061
1345	0.0243	0.704±0.041
1415	0.0198	0.574±0.038
1505	0.0145	0.421±0.074
1645	0.0129	0.374±0 055
1817	0.0102	0.296±0.082

A value for the isotope-effect parameter associated solely with the high-temperature mechanism must be known to determine which mechanism of diffusion is predominant at high temperatures. It is difficult to estimate this value because of the large errors associated with each value. By assuming that the fraction of the measured values of the isotope-effect parameter contributed by the high-temperature mechanism is directly proportional to the fractional contribution of the high-temperature diffusion mechanism to the measured diffusion coefficients, a value for the isotope-

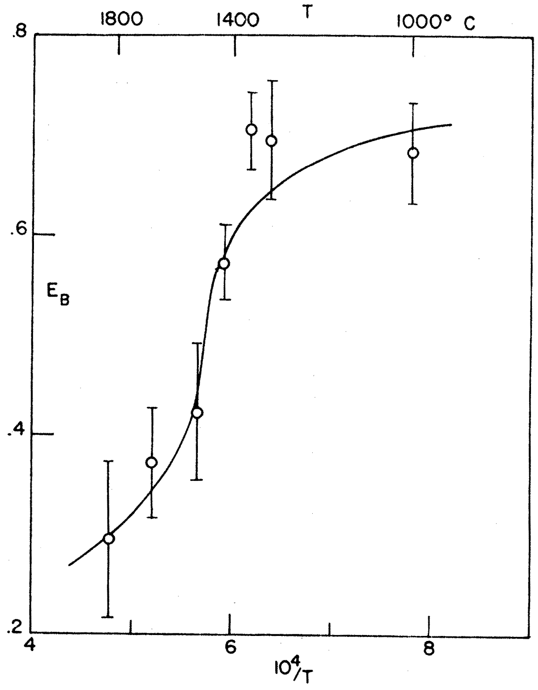

FIG. 6. Temperature dependence of the isotope-effect parameter E_B for Fe^{55} and Fe^{59} in V. (Lower abscissa is in °K^{-1}.)

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[17] D. Graham, Bull. Am. Phys. Soc. 11, 331 (1966).

effect parameter of approximately 0.2 results. This would give limiting values for the high-temperature mechanism of 1.0 and 0.2 or 0.2 and 1.0 for the correlation factor and ΔK, respectively.

Two mechanisms of diffusion, interstitialcies and divacancies, seem compatible with the values of the isotope-effect parameter at high temperatures. Several other mechanisms of diffusion, however, can be eliminated as possibilities. Ring mechanisms involving four or more atoms, using Eqs. (4) and Eq. (2), would yield values of the isotope-effect parameter greater than 1.0. Since the maximum value for both the correlation factor and ΔK is 1.0, ring mechanisms of four or more atoms are not possible. Diffusion by an interstitial mechanism is eliminated by the small values of the isotope-effect parameter. The correlation factor for interstitial diffusion is 1.0; and in cases where this mechanism is clearly operative, the value of ΔK is very near unity.

Correlation factors for interstitialcy diffusion in the body-centered cubic lattice can take on a range of values: 0.0 or 1.0 for octahedral sites and from 0.66 to 1.0 for tetrahedral sites. Diffusion from either site may have a value of ΔK of 0.5 or less. This mechanism clearly cannot be ruled out as a possibility for the high-temperature diffusion process on the basis of the present results.

There is little support for self-diffusion by an interstitialcy mechanism in the body-centered cubic lattice, although there is strong support for this mechanism in the silver halides.[18] The possibility of interstitialcy diffusion has been discussed for alpha iron by Johnson[19] and for sodium by Barr and Mundy.[20] The latter authors point out that both the octahedral and tetrahedral sites are adjacent to similar sites, and it is not clear why interstitialcy diffusion should be preferred to interstitial diffusion. Furthermore, the tetrahedral site, the largest interstitial site, has a radius less than 30% of that of the solvent atom. From size considerations alone it is hard to understand how self-diffusion could occur by any interstitial process unless the diffusing atom is heavily ionized.

Another possible mechanism is divacancy diffusion. Recently, an approximate calculation of the correlation factor for this mechanism in the body-centered cubic lattice yielded a value of close to 0.5.[21] This value is reasonable with respect to divacancy correlation factors calculated for other lattice structures: 0.62 for a NaCl structure with like atoms diffusion on each site[22] and 0.475 for the face-centered cubic lattice.[23] If relaxation of atoms surrounding the divacancy occurs, the value of ΔK will be less than unity and could be considerably less.

Johnson[19] has calculated that three possible divacancy configurations exist in the body-centered cubic lattice. These consist of single vacancies which are located on first-nearest-neighbor, second-nearest-neighbor, or third-nearest-neighbor sites. The second-nearest-neighbor divacancy is the most important for diffusion in this model. Migration of this divacanancy is accomplished by motion of each of the component vacancies through either the first-nearest-neighbor site or the fourth-nearest-neighbor site, returning in each case to a second-nearest-neighbor site. There are, thus, three configurations of this divacancy seen before (or after) and during the jump process. These configurations plus the relatively large number of nearest-neighbor atoms to the vacancies give some basis for the high D_0 factors observed in this work and for self-diffusion in vanadium: both the configuration and vibrational components of the entropy should be significantly larger than for one divacancy configuration.

The activation energy for diffusion by divacancies, Q^d, in a body-centered cubic lattice has been estimated by Peart and Askill[10] as

$$Q^d = 1.54 Q^s, \tag{7}$$

where Q^s is the activation energy of diffusion for a single vacancy mechanism. This expression results from the relation

$$Q^d = 2Q_f{}^s - E_B + Q_m{}^d, \tag{8}$$

where E_B is the binding energy of the divacancy and the subscripts f and m refer to formation and motion, respectively. They have estimated that

$$E_B = 0.1 Q_f{}^s = 0.06 Q^s$$

and

$$Q_m{}^d = Q_m{}^s = 0.4 Q^s,$$

based on the measured values of these quantities observed in several body-centered cubic metals. Using the value for the activation energy for low temperatures measured in this work, Eq. (7) yields an activation energy of 104 000 cal/mole which is very close to the activation energy measured in this experiment for D_{high} of 101 500 cal/mole. Peart and Askill also predict a value of about 2000 cm²/sec for D_0 for divacancies in vanadium, which is again very close to that observed for $D_{0,\mathrm{high}} = 2280$. This agreement between the measured values and the predicted values confirms that the divacancy mechanism must be considered as the possible high-temperature diffusion mechanism.

The conclusion reached from the present work is that two competing mechanisms of diffusion occur in vanadium, one being diffusion by single vacancies and the other quite probably a divacancy mechanism.

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Recent data by Murdock and McHargue[24] on the diffusion of Ti^{44} in vanadium and a series of vanadium-titanium alloys, ranging from 10 at.% titanium in vanadium to 10 at.% vanadium in titanium in steps of 10 at.% titanium, show that the temperature dependence of diffusion varies continuously with composition from the sharp change of slope in the $\log D$ versus $1/T$ plot in pure vanadium to a continuously curving plot for titanium. Thus, it can be inferred that two mechanisms of diffusion also operate in titanium and possibly in all of the anomalous metals.

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Band Structure and Electronic Properties of Silver

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A band-structure calculation for silver has been made using Mueller's interpolation scheme. The first-principles calculation by Segall has been adjusted to give better agreement with experiment, and a set of parameters derived to fit these adjusted bands. A density-of-states calculation using these parameters confirms deductions from experimental work using the photoelectric effect which suggest two main peaks in the *d*-band region. However, we find an additional low-energy peak which has not been observed experimentally and no evidence of structure near the Fermi level. The Fermi surface is computed after a recalculation of the Fermi energy which agrees with Segall's results. Reasonable correlation with the experimental dimensions of the Fermi surface is obtained. Finally, various effective masses are calculated. The value obtained for the electronic specific heat suggests that electron-phonon enhancement is somewhat smaller in silver than in copper.

1. INTRODUCTION

SEVERAL interpolation schemes have been constructed in recent years in an attempt to describe the energy bands of noble and transition metals.[1–3] That by Mueller[3] seems to be the most plausible physically and can actually be derived, subject to various approximations, from the Green's functions (or KKR[4]) theory of energy bands.[5–7]

The important point about an interpolation scheme is that from a relatively small amount of data—perhaps a first-principles calculation of eigenvalues at symmetry points in the Brillouin zone, or, alternatively, an experimentally determined Fermi surface—one can derive parameters for use in the interpolation scheme and then use these same parameters to extend the results to any part of the Brillouin zone. This process greatly facilitates calculation of such quantities as the electronic density of states, effective masses, etc. General considerations as to the philosophy of using such interpolation schemes have been discussed by Phillips.[8]

In this paper we describe how a one-electron band structure for silver has been obtained and show that this structure will predict various electronic quantities in reasonable agreement with experiment. The work described is a preliminary to studies of noble–transition-metal alloys, in particular those of the silver-palladium series.

2. CALCULATED SILVER BAND STRUCTURE

A. Previous Band Calculations

The only first-principles calculation for silver appears to be that due to Segall.[9] For reasons explained in his paper Segall did not claim great accuracy and, indeed, although the general shape of his bands are in qualitative agreement with those of the similar metal copper (except that in silver the *d* bands are derived from the 4*d*, rather than the 3*d*, atomic levels), some of the more quantitative features of the bands are plainly incorrect. In particular, in neither of his calculations, using two different potentials, was Segall able to predict the height of the *d* bands relative to the conduction bands so as to agree with the (admittedly tentative) interpretation of optical data. These data would place the

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