Isotope effect in chromium self-diffusion*

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(Received 20 October 1975)

The diffusion of ^{51}Cr in chromium has been measured between 1100 and 1820°C, and the data fit the Arrhenius relation $D = 970\exp(-104\,000/RT)$ cm^{2}sec^{-1}. Isotope-effect measurements, using isotopes ^{48}Cr and ^{51}Cr, have been made over the temperature range 1440–1810°C. The isotope effect decreases as the temperature increases in a manner similar to that found for sodium and iron in the same homologous temperature range. The large activation energy for diffusion and the low values of the isotope effect could be predominantly the result of a divacancy mechanism of diffusion over the measured temperature range.

INTRODUCTION

The interpretation of self-diffusion measurements in body-centered-cubic (bcc) metals has proven more difficult than for face-centered-cubic (fcc) metals.[1-4] Self-diffusion in fcc metals has been interpreted to be the result of atomic transport predominantly by means of single vacancies with a contribution from divacancies in some metals at temperatures close to the melting point. This interpretation has been considerably aided by such measurements as the isotope effect for self-diffusion, dilatometry, quenching, positron annihilation, and nuclear-magnetic-resonance experiments.[5,6] Also the single/divacancy interpretation has been applied to much of the data for self-diffusion in bcc metals.[7-9] The analyses are difficult because, for most bcc metals, the diffusion data are not sufficiently accurate, and isotope-effect experiments have not been made. The accuracy is limited because of the experimental requirements of high temperatures and clean environments for bcc transition metals. This, in turn, has also limited the quantity and quality of the other experimental data, which proved so helpful in the interpretation of the data on defects and diffusion in fcc metals.

Because of the experimental difficulties associated with bcc transition metals, the most extensively studied diffusion properties in bcc metals have been in sodium.[10] The interpretation of the sodium data has not been without ambiguity,[11-18] and the complexity may be typical of other bcc metals. The majority of the interpretations[11-18] indicate that the single/divacancy mechanism can account for most of the sodium data from both diffusion[10] and dilatometric measurements.[19] Some of the ambiguity has arisen from the difficulty encountered in the interpretation of the isotope-effect measurements.

The equation for the isotope effect can be written in the following general form:

$$(D_\alpha/D_\beta - 1) = f\Delta K\left[(m_\beta/m_\alpha)^{1/2} - 1\right],\qquad(1)$$

where D_α, m_α and D_β, m_β refer to the diffusion coefficient and mass of the α and β isotope, respectively; f is the correlation factor; and ΔK is interpreted as that fraction of the total kinetic energy of the migrating atom at the saddle point which is associated with motion in the jump direction. For self-diffusion in close-packed metals, f is a geometric factor dependent only on the crystal structure and the atomic jump process. Measurements of D_α/D_β yield the product $f\Delta K$; thus, if ΔK is close to unity, the experimental results yield a value of f that serves to identify the diffusion mechanism. Measurements of the isotope effect in bcc metals (sodium[10] and α- and δ-iron[20]) yielded not only much lower values than found for fcc metals[21] but also a much greater dependence of $f\Delta K$ on temperature. The low values have been explained in terms of low values of ΔK.[14-17,22] The large temperature dependence can be explained in terms of the several different divacancy jump paths that result in a temperature-dependent correlation factor for divacancies f_{2v}.[16,18] In view of the similarity of the isotope-effect data for sodium and iron, the present work was undertaken to extend isotope-effect data to bcc metals with higher melting points.

We chose to examine chromium for the following reason. In the group-VIa metals, the solubility of interstitial impurities is considerably lower than for group-Va metals, and we wished to minimize the impurity problems found in the work on α-iron.[23] Neumann's survey[8] of self-diffusion in bcc metals suggested that chromium had linear Arrhenius lines with acceptable values of the preexponential factor D_0 (0.2 cm^2 sec^{-1}) and the activation energy Q (73.7 kcal/mole). The isotope-effect measurements required two isotopes that could be readily distinguished, and the isotopes ^{51}Cr and ^{48}Cr satisfied, with some experimental difficulties, these requirements.

Measurements of chromium self-diffusion[24-31] have shown a much greater range of Arrhenius expressions than those found for other *bcc* metals.

Most of the work earlier than 1962 suffers from three problems. (i) The surface decreases or residual-activity methods were used with ^{51}Cr as the radioisotope. Since ^{51}Cr emits two types of radiation with quite different absorption coefficients (vanadium x rays and 0.31-MeV γ rays), difficulties will be encountered with absorption methods unless special care is taken. (ii) The lowest temperatures at which the measurements were made were sufficiently low to show significant grain-boundary contributions in the polycrystalline samples used. (iii) The range of temperatures was too narrow and the highest temperature too far below the melting point[32] for an accurate determination of D_0 and Q.

The data of Hagel[28] and Askill and Tomlin[30] are in close agreement and indicate that chromium exhibits "normal" bcc diffusion ($D_0 \sim 0.2$ cm^2 sec^{-1} and $Q \sim 73$ kcal/mole). "Normal" is used for those bcc metals with diffusion properties that have linear Arrhenius relations and have values of D_0 between 0.1 and 10 cm^2 sec^{-1} and $Q/T_m \sim 35$ cal/mole K^{-1} (T_m is the melting temperature). Two problems have arisen since Askill and Tomlin's work. Neumann[8] in his single/divacancy analysis of all bcc metal diffusion data found that chromium was one metal which did not fit the pattern. The single activation energy found by experiment was in much better agreement with the theoretical value for Q_{2v} than for Q_{1v}. In 1971, Askill[31] repeated his measurements on chromiun over the temperature range of 1000–1870 °C. He obtained considerably lower diffusion coefficients, a higher activation energy value (81 kcal/mole) between 1000 and 1775 °C, and an even higher activation energy above 1775 °C.

The problems associated with previous chromium self-diffusion measurements suggested the need for the measurements to be repeated on single crystals of high-purity chromium. The present paper describes such measurements made over a temperature range 1100–1820 °C and isotope-effect measurements between 1440 and 1810 °C.

EXPERIMENTAL METHODS

The results of the diffusion measurements presented in the present paper proved difficult to interpret, and, for this reason, the experimental techniques are given in some detail. The basic method used was to observe the diffusion of a thin surface layer of radiotracer by sectioning. The solution of the diffusion equation for these experimental conditions is

$$c_x = [S/2 \, (\pi D t)^{1/2}] e^{-x^2/4Dt} \, , \tag{2}$$

where c_x is the specific activity of the tracer at a distance x from the surface, t is the time of

anneal, D is the diffusion coefficient, and S is the concentration per unit area at $x=0$ and $t=0$.

A. Materials

Single-crystal boules of pure chromium ($\frac{1}{4}$-in. diam, 2 in. long, and 99.995% purity) were obtained from Imanco Corp., New York. The boules were spark cut into $\frac{1}{8}$-in.-thick disks. The flat sides of the disks were ground parallel with 4/0 grade emery paper, and then the surface were polished with a Syntron Vibratory polisher, using 0.3-μm alumina powder suspended in ethylene glycol. Surface irregularities were reduced to <0.1 μm, and Laue photographs confirmed that each sample was a single crystal.

Measurement of the isotope effect of chromium self-diffusion required the use of the radioisotopes ^{51}Cr, ^{48}Cr, and ^{48}V. The ^{51}Cr and ^{48}V were obtained from International Chemical and Nuclear Corp., Irvine, Calif.; both isotopes showed no radioactive impurities on a Ge(Li) γ spectrometer. The ^{48}Cr was prepared by the reaction ^{48}Ti(^{3}He, 3n)^{48}Cr, and subsequent chemical separation.[33] The use of ^{48}Cr isotope for diffusion measurements is complicated by the growth of the radioactive daughter ^{48}V and the presence of ^{51}Cr isotope created in the ^{48}Cr production process. The measurement of the half-lives of these isotopes [$T_{1/2}(^{51}$Cr$)=27.703$ days, $T_{1/2}(^{48}$V$)=15.976$ days, and $T_{1/2}(^{48}$Cr$)=21.56$ h] has been described in an earlier paper.[33]

B. Diffusion measurements

The radioisotopes (^{51}Cr, ^{48}Cr, and ^{48}V) were obtained as chlorides in dilute hydrochloric acid. These chlorides were dried and redissolved in water prior to drying on the polished surface of the chromium samples. The specific activities of all radioisotopes were sufficiently high so that the thickness of the deposited layer was $\ll 0.1$ $(Dt)^{1/2}$. The samples were placed in tantalum capsules under $\frac{1}{3}$ atm of an argon-helium gas mixture and closed by means of arc welding. The encapsulation minimized surface evaporation from the sample. The samples were prevented from direct contact with the tantalum by rings and disks of sapphire. Direct contact would have allowed a chromium-tantalum eutectic to form at the higher anneal temperatures. Some samples were preannealed in the tantalum capsules for 6 h at temperatures within 100 °C of the melting point. The preannealing appeared to have no effect on the penetration profiles nor on the diffusion coefficients obtained from the profiles.

The diffusion anneals at temperatures 1322 °C and above were made in a vacuum furnace. The temperature was measured with an optical pyrometer focused on a blackbody hole located directly

below the tantalum capsule. The pyrometer was calibrated, through the window of the furnace, against a standard tungsten strip lamp. Errors due to the temperature difference between the sample and the blackbody hole and also the metering effect of the small aperture of the furnace window were taken into account. The absolute temperature above 1322 °C could be in error by ±10 °C. The capsule temperature was monitored continuously with a thermocouple $(W + 3\% Re/W + 25\% Re)$, using a chart recorder. Although the agreement between the temperature given by the pyrometer and that given by a calibrated thermocouple was within 10 °C at the beginning of anneal, the thermocouple frequently "drifted." The thermocouple readings were only used to determine the correction to the anneal time due to the "heat-up" and "quench" periods.

The diffusion anneals at temperatures 1225 °C and below were made in a platinum-wound furnace. Five of the eight anneals were made with samples encapsulated only in sealed quartz tubes under $\frac{1}{3}$ atm of argon gas. The zirconium chips that were included in the capsules did not prevent some oxidation of the sample surfaces. To test whether this oxidation was affecting the measured diffusion coefficients, the anneals at 1225, 1156, and 1096 °C were made with the samples encapsulated in the same manner as those for the higher-temperature anneals. The tantalum capsules were, in turn, encapsulated under argon gas in quartz tubes to prevent oxidation. The samples, from these anneals, were found to be bright and shiny following the anneal, as were all the samples from the high-temperature anneals.

Experiments on self-diffusion in α-iron[23] have indicated that small increases in the interstitial content (~ 10 wt ppm to ~ 120 wt ppm) enhanced the self-diffusion coefficient by a factor of 40. Chromium samples were analyzed by fusion analysis to determine the hydrogen, oxygen, and nitrogen content. In all analyses, the hydrogen and nitrogen content was below 10 wt ppm. Samples that had not been annealed showed oxygen contents of ~ 160 wt ppm. Samples taken after the diffusion anneals showed considerably less oxygen (< 30 wt ppm). Although at this level of oxygen content some scatter in the data occurred; the analyses appeared to show that the higher the anneal temperature the lower the oxygen content of the sample. This information could be explained if the tantalum capsule was acting as a "getter" for oxygen diffusing from the chromium samples.

After the anneal, the samples were reduced in diameter on a lathe so that the penetration profile was not affected by any vapor or surface transport. The samples were sectioned by grinding on 4/0 paper on a precision parallel grinder, and the

papers were uniformly folded and placed in small counting bottles. The sample was weighed after each successive layer was removed. (After weighing the sample was washed with distilled water and cleaned ultrasonically. The "wash water" was added to the bottle containing the paper for that section.) The thickness of each section was determined from the weight of the section, the measured area, and the density of the sample. Each section was counted in a well-type NaI(Tl) crystal scintillation counter to 10^5 counts. The penetration of the radiotracers was determined over two or three orders of magnitude in the specific activity.

Measurements of chromium self-diffusion, with the ^{51}Cr isotope deposited as an evaporated metal film, were made at 1114, 1208, 1374, 1407, and 1645 °C. The ^{51}Cr was made by irradiating pure natural chromium in the Argonne CP-5 reactor. Analysis of the γ-spectrum, using a Ge(Li) detector, showed no detectable radioactive impurities. No measurable difference was found in the diffusion coefficients obtained from ^{51}Cr evaporated as metal and those obtained using ^{51}CrCl$_3$ deposited as salt. The latter method relies on the reaction

$$2CrCl_3 \rightarrow 2Cr + 3Cl_2 \uparrow$$
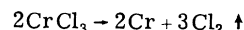
on the sample surface. We attempted to plate chromium metal from chromium salt, but the low concentrations of chromium that were necessary to maintain the validity of Eq. (2) made plating inefficient and unreliable. The isotope-effect measurements were possible only because the surface reaction proved viable.

C. Isotope-effect measurements

Measurements of the isotope effect in diffusion are usually made by the simultaneous diffusion of two isotopes, α and β, into a sample. The ratio of the specific activities (c_α/c_β) as a function of penetration (c_α) can be shown from Eq. (2) to be

$$\ln(c_\alpha/c_\beta) = (\text{const}) - \ln c_\alpha \ (D_\alpha/D_\beta - 1) \ . \tag{3}$$

A plot of $\ln(c_\alpha/c_\beta)$ vs $\ln(c_\alpha)$ allows a determination of the relative diffusion coefficient $[(D_\alpha/D_\beta) - 1]$. The accuracy of the measurement of $[(D_\alpha/D_\beta) - 1]$ is determined by the accuracy of (c_α/c_β) over a range of (c_α). The ratio of (c_α/c_β) has frequently been determined to within 0.1% by a half-life separation of the γ activities of the two isotopes.[10,20,34] The specific activity of a given section c changes with time as

$$c = c_\alpha \ e^{-\lambda_\alpha t} + c_\beta \ e^{-\lambda_\beta t} \ , \tag{4}$$

where t is the elapsed time from an arbitrary time zero, and λ_α and λ_β are the decay constants of the respective isotopes. The ratio (c_α/c_β) at
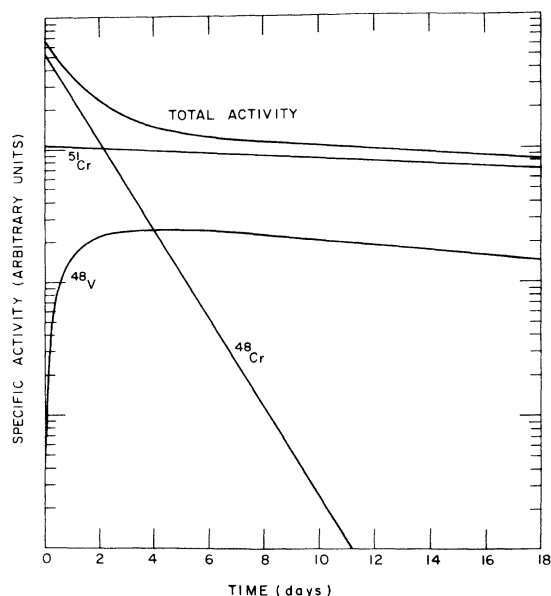
FIG. 1. Total γ activity as a function of time for specific activities of ^{51}Cr and ^{48}Cr used in a typical isotope-effect experiment.

the start of counting is usually adjusted to be approximately six, and the decay is followed for at least five times the half-life of the short-lived isotope $[5 \times T_{1/2}(\alpha)]$.

Measurement of the isotope effect for chromium self-diffusion was made with the isotopes ^{51}Cr $(T_{1/2} = 27.703$ days) and ^{48}Cr $(T_{1/2} = 21.56$ h).[33] The usual half-life separation of the isotopes was complicated by the decay of the ^{48}Cr isotope to the ^{48}V daughter isotope $(T_{1/2} = 15.976$ days). After $5 \times T_{1/2}(^{48}$Cr$)$, the count rate from the ^{48}V daughter is of the same order as that from the ^{48}Cr isotope (Fig. 1); therefore, the usual half-life separation is not possible.

When the half-lives of the available isotopes are either too similar or too long to make an accurate half-life separation, the different γ spectra of the isotopes can, in some cases, allow a separation by energy discrimination.[35] The γ-spectra of the isotopes ^{51}Cr, ^{48}Cr, and ^{48}V are shown in Fig. 2. A separation of the chromium isotopes by energy is feasible by using pure ^{51}Cr and ^{48}V as standards. The pulses from the amplifier were fed simultaneously to two lower-level discriminations (LL I and LL II in Fig. 2).

If $A = $ (count rate in LL II/count rate in LL I) for pure ^{51}Cr and $B = $ (count rate in LL II/count rate in LL I) for pure ^{48}V, all counts are corrected for dead time and background, and then, for a sample containing X counts of ^{51}Cr and Y counts of ^{48}V in LL I, $X + Y$ is the count rate in LL I and $AX + BY$ is the count rate in LL II. The ratios A and B were determined from pure ^{51}Cr and ^{48}V

standards, and the equations allow the relative concentration of chromium and vanadium to be determined.

The energy-separation method was tested by simultaneously diffusing approximately equal activities of ^{51}Cr and ^{48}V. The impurity diffusion of ^{48}V in chromium was significantly faster than chromium self-diffusion. If the impurity diffusion had been significantly slower than chromium self-diffusion, the isotope-effect measurements could have been made using a simple half-life separation method. Accurate knowledge of the ratio of the vanadium-impurity diffusion to chromium self-diffusion would have permitted a small correction to be made for the ^{48}V counts. The measurements made using ^{51}Cr and ^{48}V isotopes showed that the faster diffusion rate of ^{48}V would lead to a sufficiently large correction which would result in inaccurate isotope-effect measurements.

The discriminator levels were set so that the values of A were $\sim 3 \times 10^{-4}$ and the values of B ~ 0.070; the settings were at points in the spectra where "drift" in the equipment would cause minimal effect. The LL II level (Fig. 2) was set higher than would appear necessary to reduce the value of A determined for the pure ^{51}Cr isotope. The value of A for ^{48}Cr was an order of magnitude larger because of the 0.425-MeV sum peak, and the form of the decay scheme made an accurate determination difficult. A change in the value of A from 3×10^{-4} to 3×10^{-2} would change the mea-
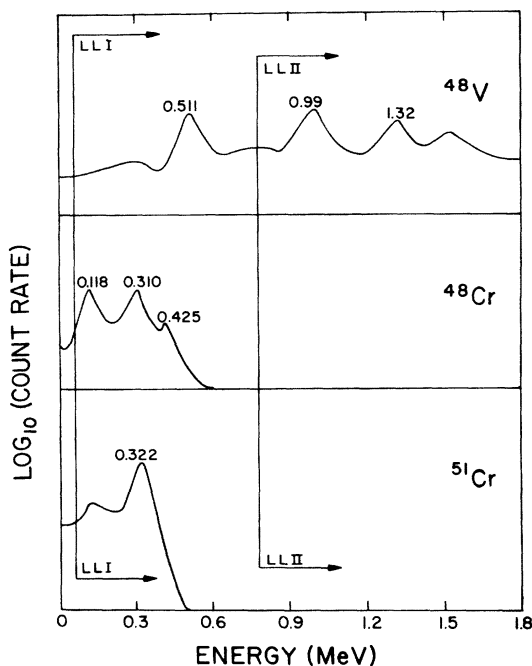

FIG. 2. γ-ray spectra of ^{51}Cr, ^{48}Cr, and ^{48}V as measured in the present experiments.

sured isotope effects by < 0.5%. Pure ^{51}Cr standards were used in the counting procedure to determine A and to watch for drift during the counting observation period. The sample preparation and annealing were the same as described in the section on diffusion methods. The samples were sectioned on tantalum foil coated with diamond powder in water. After each section was taken, the foil was uniformly folded, placed in a counting vial, and counted. These counts were used to determine the values of the specific activity c_α. After this initial count, the contents of each counting vial were washed into a 250-ml beaker, and all the chromium was dissolved in 2N HCl. The tantalum foils were removed, and the volume of solution was reduced to 2 cm^3 by successive drying and redissolution. In this manner, the vials from each section finally contained > 98% of their original chromium content which was dissolved in 2 cm^3 of 2N HCl. This sectioning procedure was used because we believed that an isotope-separation technique which needed two separations and used isotopes with relatively low γ energies would require that each section had a uniform counting geometry. We have not tested the necessity of the requirement. All vials were counted to 10^6 counts, and corrections were made for counter dead time and background. The counter dead times (~2.5×10^{-8} sec) were measured to within 10%, and the "hot" sections were diluted to 5×10^5 counts/min. Standard vials were prepared from pure ^{51}Cr and pure ^{48}V isotopes, with counting rates that spanned the counting rates of the vials from the diffusion profile sections. From an aliquot of one of the first sections, a set of

TABLE I. Diffusion of ^{51}Cr and ^{48}V in chromium as a function of temperature.

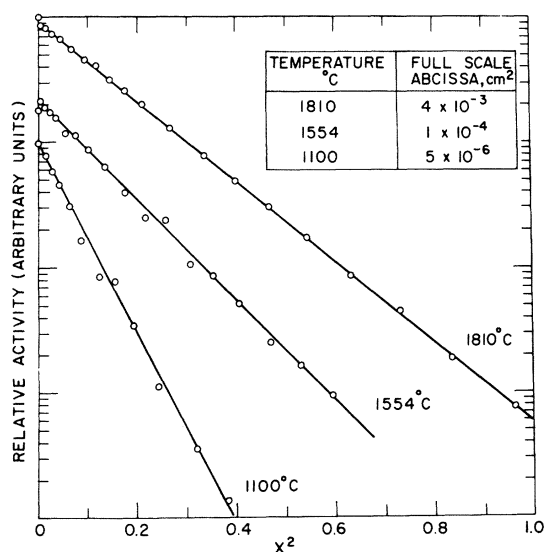| Temperature (°C)	D (cm^2 sec^{-1})	
	^{51}Cr/Cr	^{48}V/Cr
1820	$1.22 \pm 0.02 \times 10^{-8}$	
1810	$1.19 \pm 0.01 \times 10^{-8}$	
1787	$7.86 \pm 0.04 \times 10^{-9}$	
1768	$6.67 \pm 0.09 \times 10^{-9}$	$8.15 \pm 0.09 \times 10^{-9}$
1768	$6.58 \pm 0.08 \times 10^{-9}$	$7.99 \pm 0.14 \times 10^{-9}$
1751	$6.12 \pm 0.07 \times 10^{-9}$	
1723	$3.49 \pm 0.02 \times 10^{-9}$	
1684	$2.03 \pm 0.02 \times 10^{-9}$	$2.55 \pm 0.03 \times 10^{-9}$
1684	$1.91 \pm 0.02 \times 10^{-9}$	$2.50 \pm 0.02 \times 10^{-9}$
1649	$1.33 \pm 0.04 \times 10^{-9}$	
1645	$8.92 \pm 0.06 \times 10^{-10}$	
1645	$1.26 \pm 0.02 \times 10^{-9}$	
1612	$9.43 \pm 0.06 \times 10^{-10}$	
1570	$3.05 \pm 0.04 \times 10^{-10}$	$3.84 \pm 0.04 \times 10^{-10}$
1554	$3.02 \pm 0.02 \times 10^{-10}$	
1554	$2.96 \pm 0.02 \times 10^{-10}$	
1532	$2.86 \pm 0.04 \times 10^{-10}$	
1492	$1.10 \pm 0.01 \times 10^{-10}$	
1441	$5.27 \pm 0.11 \times 10^{-11}$	
1407	$2.99 \pm 0.07 \times 10^{-11}$	
1407	$2.25 \pm 0.14 \times 10^{-11}$	
1374	$1.36 \pm 0.02 \times 10^{-11}$	
1322	$6.98 \pm 0.14 \times 10^{-12}$	$1.03 \pm 0.02 \times 10^{-11}$
1225	$5.32 \pm 0.12 \times 10^{-13}$	
1208	$6.70 \pm 0.20 \times 10^{-13}$	
1208	$3.40 \pm 0.20 \times 10^{-13}$	
1156	$7.25 \pm 0.12 \times 10^{-14}$	
1114	$7.40 \pm 0.50 \times 10^{-14}$	
1100	$2.16 \pm 0.23 \times 10^{-14}$	
1100	$1.80 \pm 0.17 \times 10^{-14}$	
1096	$2.56 \pm 0.16 \times 10^{-14}$	

TEMPERATURE °C	FULL SCALE ABCISSA, cm^2
1810	4×10^{-3}
1554	1×10^{-4}
1100	5×10^{-6}

FIG. 3. Concentration profiles for the diffusion of ^{51}Cr into chromium.

null-effect counting vials was prepared. In this set, the ratio of ^{51}Cr to ^{48}Cr remains the same in each vial, but the total activity spans the count rates of the "sections." Standard, section, and null-effect vials were counted in a somewhat random order ten or more times during the course of a week. The standard vials were used to test the effects of discriminator drift during this period and also any count-rate dependence of A or B. The null-effect vials were used to test whether the isotopic ratios determined by the separation procedure were count-rate dependent.

EXPERIMENTAL RESULTS

A. Diffusion measurements

Figure 3 shows examples of penetration plots in $\log_{10}(c)$ vs x^2 for chromium self-diffusion. The lowest temperature (1100 °C) was limited by the grinding technique (~1-μm sections). Values of the diffusion coefficient were obtained from a least-squares fit of the data to Eq. (2). These values are listed in Table I and plotted in Fig. 4.
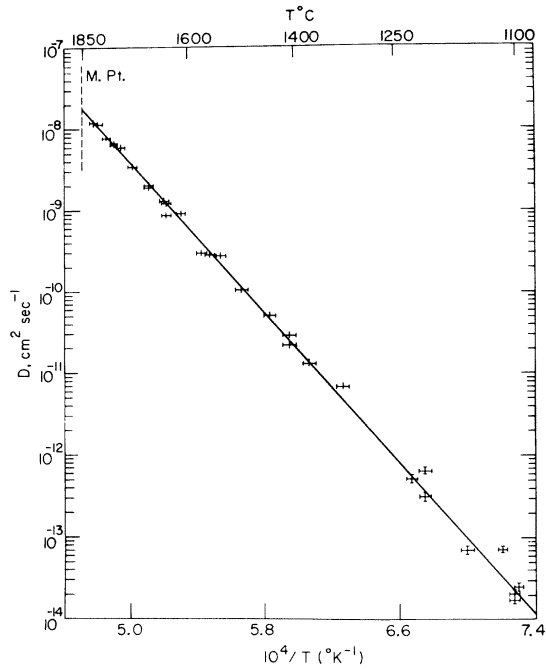
FIG. 4. Diffusion of ^{51}Cr into chromium as a function of temperature.

The errors in D arise from the scatter in the penetration profile and the measurement of anneal time. The largest error is in the measurement of temperature. These errors were $\pm 10\,^{\circ}$C for all anneals, except for the three lowest temperatures which were $\pm 5\,^{\circ}$C. The diffusion coefficients fit the Arrhenius relation

$$D = 970 \exp\left(-\frac{104\,000 \pm 1000}{RT}\right) \text{cm}^2 \text{sec}^{-1} , \qquad (5)$$

where the activation energy is expressed in cal/mole. The entropy of activation ΔS can be obtained from the equation

$$D_0 = \gamma a^2 \nu f e^{\Delta S/k} , \qquad (6)$$

where γ is a geometrical constant that depends on the cell geometry and the assumed jump mechanism, ν is an average vibration frequency, a is the lattice parameter, and k is Boltzmann's constant. If we assume a single-vacancy mechanism, $\gamma = 1$, $f = 0.727$, $a = 2.885 \times 10^{-8}$ cm, and $\nu = 10^{13}$ sec^{-1} from Eq. (6) the entropy is $12k$.

The values of D for ^{48}V diffusing in chromium are also given in Table I. Each of these measurements was obtained from samples where ^{51}Cr and ^{48}V were diffused simultaneously so that the ratio of the impurity to the self-diffusion coefficient is more accurate than the absolute values. The ratios were used to determine the activation energy for ^{48}V diffusion in chromium of 101 kcal/mole.
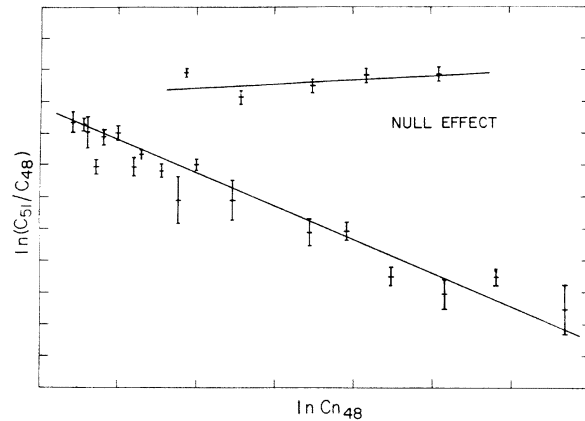

FIG. 5. Diffusion of ^{51}Cr and ^{48}Cr in chromium. Each division on the ordinate is 0.01. Each division on the abscissa is 1.0.

B. Isotope-effect measurements

An example of the experimental plot $\ln(c_{51}/c_{48})$ vs $\ln c_{48}$ is shown in Fig. 5. The scatter of data is greater than found[10,28,34] for isotope separations made by the half-life separation technique. The double separation technique is believed to be the cause of the scatter. The results of the null-effect experiment appropriate to the diffusion data are shown in Fig. 5. Table II shows the values of $f\Delta K$ determined from the slopes of the $\ln(c_{51}/c_{48})$-vs $\ln(c_{48})$ data. The error in $f\Delta K$ quoted in the table includes the error in determining $f\Delta K$ from the data and any error due to a nonzero null-effect slope. The table also includes values of the ratio T_m/T, the ratio of the chromium melting temperatures to the temperature of the diffusion anneal. A plot of $f\Delta K$ versus the homologous temperature T_m/T (Fig. 6) allows a comparison of the chromium and sodium self-diffusion data.[10] The measured melting temperature of chromium obtained by different observers has ranged from 1830 to 1900 $^{\circ}$C.[32] We have used a value of 1852.5 $^{\circ}$C in the tabulation in Table II. The 1852.5 $^{\circ}$C value is a mean of the value of

TABLE II. Isotope effect for diffusion of ^{51}Cr/^{48}Cr in chromium as a function of temperature.

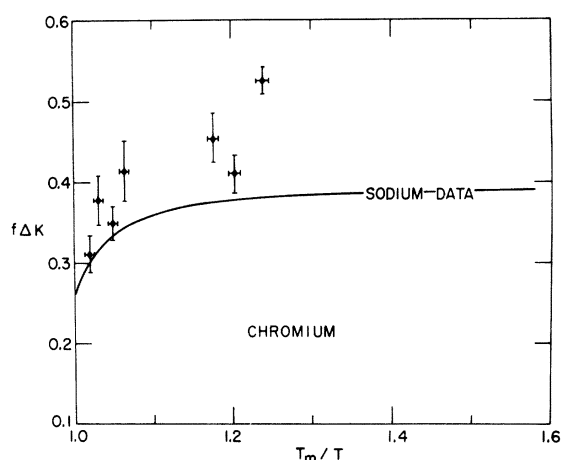| Temperature (°C)	$f\Delta K$	$\dfrac{T_m}{T}$
1810	0.31 ± 0.02	1.020
1787	0.38 ± 0.03	1.032
1751	0.35 ± 0.02	1.050
1723	0.41 ± 0.04	1.065
1532	0.45 ± 0.03	1.177
1492	0.41 ± 0.02	1.204
1441	0.52 ± 0.02	1.240

FIG. 6. Variation of $f\Delta K$ with temperature for chromium. The solid line is a best fit to the sodium data from Ref. 10.

Carlile *et al.* and Greenaway.[32] On two occasions, we accidentally melted samples; the temperature was estimated to be between 1840 and 1860 °C.

The values of $f\Delta K$ for the two lowest-temperature anneals were obtained after omission of the last three data points from the $\ln(c_{51}/c_{48})$-vs-$\ln(c_{48})$ plot. The $\ln(c_{51})$-vs-x^2 data for the 1492 °C anneal were linear for a drop in specific activity of 150, and then the slope abruptly decreased. At the same point in the $\ln(c_{51}/c_{48})$-vs-$\ln(c_{48})$ plot, the slope abruptly increased. The 1440 °C anneal showed exactly the opposite effect for both slopes. The effect of including the last three points raises $f\Delta K$ (1492 °C) and lowers $f\Delta K$ (1441 °C), thus reducing the scatter of data in Fig. 6. The three points were omitted because we cannot understand why the breaks in the slopes should occur.

We examined the effect of small changes in the decay constant (λ) of ^{48}Cr on the measured value of $f\Delta K$. A 1% change in λ causes a 10% change in $f\Delta K$. Our measurements[33] of $T_{1/2}$ (^{48}Cr) showed an error of 0.14%, and thus the resultant error in $f\Delta K$ was considerably smaller than the present experimental scatter.

DISCUSSION

The present work introduces additional anomalies into the data for diffusion in bcc metals. The values of the preexponential factor ($D_0 = 970$ cm^2 sec^{-1}) and the activation energy ($Q = 49$ T_m) are unusually high when compared with the values for most other metals. The low values and strong temperature dependence of $f\Delta K$ in the data for sodium[10] was accompanied by curvature in the Arrhenius expression. The present isotope-effect results (Fig. 6) are similar to those for sodi-

um, but the present Arrhenius line is straight within the experimental error. A single-divacancy interpretation of the present data would be satisfactory for the isotope-effect data but would indicate that measurable curvature should be present in the Arrhenius plot. Before presenting a possible interpretation of these anomalies, we wish to discuss briefly why we believe the present data are not artifacts of the experiments. The high values of D_0 and Q could be the result of the enhancement, by vapor transport, of the measured values of D at high temperatures. This effect could be greater for chromium than for other metals because of the large vapor pressure. However, the values of D at high temperatures are not unusually high compared with values for other metals.

A comparison of the more-recent chromium self-diffusion data[28,30,31] with the present work shows that, at high (~1600 °C) temperatures, all workers obtained similar values for the diffusion coefficient. At lower temperatures, each succeeding experiment obtained increasingly lower values of D so that at 1200 °C the present work is an order of magnitude lower than that of Hagel.[28] These lower diffusion coefficients have resulted in higher values of D_0 and Q. [A least-squares analysis of Askill's[31] data using all points that appear to represent bulk diffusion gives $D = 17.4 \exp(- 89\,500/RT)$ cm^2 sec^{-1}.] Irmer and Feller-Kniepmeier[23] showed in their work on self-diffusion in α-iron that when the content of the interstitial impurities, oxygen and carbon, is low (of the order of, or less than, the solubility limit) an order of magnitude reduction in content leads to a similar reduction in the value of the diffusion coefficient.

Irmer and Feller-Kniepmeier also showed that, above a certain level of interstitial content, the effect appeared to saturate and additional enhancements of the diffusion coefficient were small. The saturation level could be at the solubility limit for the interstitial impurities, but the numbers are not sufficiently well defined to be certain. The analyses of the present samples made after the diffusion anneals showed that the total interstitial content was low and the oxygen content was approximately at the solubility limit for a temperature of 1200 °C.[32] The earlier work did not give the interstitial content of the samples, but, despite experimental precautions, it would appear likely that it was higher than in the present work. If the effect observed for α-iron was dependent on the reduction of the interstitial content below the solubility limit, then one would expect the present chromium self-diffusion measurements to show more deviation from the previous measurements at higher solubility limits, i.e., at higher temperature. These data show a smaller

TABLE III. Comparison of diffusion parameters for bcc transition metals.

Element	$(D_0)_1$ (cm^2 sec^{-1})	Q_{1v}/T_m (cal/mole K^{-1})	$(D_0)_2$ (cm^2 sec^{-1})	Q_{2v}/T_m (cal/mole K^{-1})	$\dfrac{(D_0)_2}{(D_0)_1}$
V	0.19	33	762	47	4×10^3
Nb	0.55	35	220	47	4×10^2
Ta	0.037	29	37	41	1×10^3
Cr	0.005	33	970	49	2×10^5

difference at higher temperatures and indicate either directly conflicting information or the interstitial content has no measurable effect on the value of the chromium self-diffusion at these higher temperatures.

A possible explanation for the high values of D_0 and Q could be that, over the entire range of temperature measurement, diffusion occurred predominantly by means of divacancies. Similar high values have been found in high-temperature measurements of vanadium self-diffusion.[36-38] The authors of the vanadium work and others[7,8,36,37] discussed the possibility of a divacancy mechanism at high temperatures, and their discussions are also applicable to the chromium data. High values of $(D_0)_{2v}$ were found in the single/divacancy analysis of bcc metal diffusion by Mehrer et al.[9] The difficulty is understanding why no curvature is apparent in the Arrhenius line, which would indicate a contribution from a single-vacancy mechanism.

An estimate of the magnitude of such a contribution was made by first determining a value of Q_{1v} by use of the following equation:

$$Q_{2v} = 2E_{1v}^f - E_{2v}^b + E_{2v}^m ,$$

where Q_{2v} is the activation energy for diffusion, E_{2v}^b is the binding energy, E_{2v}^m is the migration energy of divacancies, and E_{1v}^f is the formation energy of single vacancies. If one makes the assumptions $E_{1v}^m/E_{1v}^f = 0.45$,[39] $E_{2v}^b = 0.1\ E_{1v}^f$, and $E_{1v}^m = 22.8$ kcal/mole,[39] one obtains the value $Q_{1v} = 71.3$ kcal/mole or $Q_{1v}/T_m \sim 33$ cal/mole K^{-1}. This value of Q_{1v} was used to determine $(D_0)_{1v}$.

The value of $(D_0)_{1v} \leq 0.005$ cm^2 sec^{-1} ensures that the contribution of single vacancies to chromium self-diffusion would not be observable within the experimental scatter of the data and leads to the Arrhenius relation for single vacancies of

$$D = 0.005 \exp(-71\,300/RT)\ \text{cm}^2\text{sec}^{-1}. \qquad (7)$$

Clearly, the numbers obtained are not unique and so, as some measure of their plausibility, they are compared in Table III with the diffusion parameters obtained by Mehrer et al.[9] The values of Q/T_m for single vacancies are similar as are the values for divacancies, but the particularly large ratio of $(D_0)_{2v}/(D_0)_{1v}$ is unusual.

The preponderance of divacancies would be unique to chromium and could possibly result from weaker interatomic forces, as evidenced by the high vapor pressure. Diffusion measurements of metals in group Ia and Ib of the Periodic Table have varying amounts of curvature in their Arrhenius plots. When these plots have been analyzed for single/divacancy mechanisms one finds, in all cases, that the higher the vapor pressure the higher the divacancy contribution to diffusion.

The predominantly divacancy interpretation would require a strong temperature dependence for $f\Delta K$. This temperature dependence would arise from the two types of divacancy jumps that must be considered in the bcc lattice.[9,16,18] A stronger test of the proposed predominance of divacancies in chromium cannot be easily obtained because of the experimentally difficult requirements of the reduction of the experimental error and the extension of the measurements to lower temperatures.

ACKNOWLEDGMENTS

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