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Diffusion of zirconium in niobium: The influence of fast diffusing impurities on the self-diffusion isotope effect*

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The diffusion of ^{95}Zr in niobium was measured over the temperature range from 1923 to 2523 K. The data fit the Arrhenius relation $D = 0.85\exp(-3.93\ \mathrm{eV}/kT)\ \mathrm{cm^2\,sec^{-1}}$. The changes in the self-diffusion isotope effect caused by ultralow levels (less than 100 at. ppm) of a fast-diffusing radioactive impurity are analyzed. It is concluded that radioactive-impurity levels not easily observed by Ge(Li) detectors can introduce large errors into the measurement of the isotope effect.

I. INTRODUCTION

Measurements of the isotope effect in diffusion have proved a powerful tool for deducing details of the diffusion process. The equation for the isotope effect can be written in the general form

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

where D_α, m_α, and D_β, m_β refer to the diffusion coefficient and mass of the α and β isotopes, 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 upon the crystal structure and the atomic-jump process. Measurements of D_α/D_β combined with Eq. (1) yield the product $f\Delta K$; thus, if ΔK is assumed to be close to unity, the measurements can be used to calculate a value of f that serves to identify the diffusion mechanism. Measurements of the isotope effect in body-centered cubic (bcc) metals[1-3] have yielded not only much lower values than found for face-centered cubic (fcc) metals,[4] but also a much greater dependence of $f\Delta K$ on temperature. The temperature dependence of $f\Delta K$ in bcc niobium could in principle have been examined over a much wider temperature range than was possible in the previous investigations.[1-3]

The method frequently used for accurate determination of diffusion coefficients is the deposition of a thin layer of radioactive tracer onto one end of a sample, followed by annealing, sectioning, and analyzing each section for tracer content. This thin-film serial sectioning method usually results in a Gaussian depth dependence of the concentration, i.e.,

$$C(x) = \frac{S}{(\pi Dt)^{1/2}} \exp\left(\frac{-x^2}{4Dt}\right), \tag{2}$$

where $C(x)$ is the specific activity of the tracer at a distance x from the isotope-sample interface, t is the time of anneal, D is the diffusion coefficient, and S is the concentration per unit area at $x=0$ and $t=0$. The method yields accurate measurements of the diffusion coefficients only when the experimentally obtained concentration profiles are Gaussian.

Deviations from Gaussian behavior can occur for a number of reasons. At the initial surface, evaporation or oxidation processes can be in competition with the bulk diffusion process. A non-Gaussian "tail" on the $\ln C$ vs x^2 profile can arise from the presence of a small amount of fast-diffusing radioactive impurity. When the diffusion anneals are made at temperatures as low as half the melting temperature of the sample, the $\ln C$ vs x^2 profile may be somewhat nonlinear because of the contribution of short-circuiting paths. The magnitude of these deviations from Gaussian behavior can be small and within the scatter of the experimental data. The deviations may not be observable unless the concentration profiles are measured to a depth of $5\sqrt{Dt}$ into the sample. When concentration profiles are measured to this depth, any observed curvature can frequently be resolved into its component parts by two-exponential fitting procedures. It should be possible to distinguish between a profile that results from bulk diffusion plus a grain-boundary contribution, and one that results from bulk diffusion of two species, of which one may be a fast-diffusing radioactive contaminant. The equation for the first profile is

$$C(x) = A\exp(-Bx^2) + F\exp(-Ex^{6/5}). \tag{3}$$

The equation for the second is

$$C(x) = A\exp(-Bx^2) + G\exp(-Hx^2), \tag{4}$$

where A, B, E, F, G are fitting parameters. In practice, the scatter in the experimental data is usually too great for a statistically significant difference to be found between the fits.

To measure a small difference (1%) in the diffusion coefficients, the two isotopes α and β are commonly codiffused from a thin-surface layer and then sectioned. The relative concentration of the two isotopes is given by

$$\ln(C_\alpha/C_\beta) = \text{const} - \ln C_\alpha (D_\alpha/D_\beta - 1)\,. \qquad (5)$$

From Eq. (5) it is clear that the slope of the plot of $\ln(C_\alpha/C_\beta)$ vs $\ln C_\alpha$ is $(D_\alpha/D_\beta - 1)$. When suitable isotopes are available such that C_α/C_β can be determined in each section, then codiffusion of the isotopes provides an accurate method of determining $(D_\alpha/D_\beta - 1)$. The isotopes ^{95}Nb and ^{90}Nb could be used to measure the niobium self-diffusion isotope effect since they are readily distinguished by their difference in half-life [$T_{1/2}(^{95}\text{Nb}) = 35$ day, $T_{1/2}(^{90}\text{Nb}) = 15$ h]. In a paper[5] on niobium self-diffusion, the presence of "tails" on the concentration profiles was noted. Since the isotope was obtained by the separation of fission products containing zirconium, it was hypothesized that a fast-diffusing zirconium impurity could have caused the tails. This work checks that hypothesis and examines the effects of a fast-diffusing radioactive impurity on the accuracy of measurements of both diffusion and isotope effect.

II. EXPERIMENTAL METHODS

The experimental methods used are discussed in Ref. 5. The experiments described there used a ^{95}Nb isotope obtained from the Oak Ridge National Laboratory in the form of niobium oxalate in oxalic acid. The ^{95}Nb isotope is a daughter of ^{95}Zr which is obtained as a fission product. A γ-spectrum analysis of the ^{95}Nb isotope as supplied showed that 0.2% to 1% of the specific activity was from ^{95}Zr. The difference in the half-lives of the isotopes—$T_{1/2}(^{95}\text{Nb}) = 35$ day and $T_{1/2}(^{95}\text{Zr}) = 65$ day—means that every two months the effective concentration of ^{95}Zr has doubled relative to that of the ^{95}Nb.

Self-diffusion anneals[5] from thin films of ^{95}Nb on single-crystal niobium showed straight penetration profiles over 1.5 to 3 orders of magnitude in concentration before showing a "tail" as exemplified in Fig. 1. This tail appeared in the profiles obtained from anneals at all temperatures. Subsequent examination of the samples by scanning electron microscopy revealed no evidence of pores or holes. A γ-spectrum examination with a germanium detector was made of sections taken from a depth of approximately $3\sqrt{Dt}$ into the samples. The spectra analyses showed that the ^{95}Zr concentration was five times greater at a depth of $3\sqrt{Dt}$ than it was at the surface. Therefore, the tails were believed to be caused by fast diffusion of ^{95}Zr into the samples. Sections from the tail regions could not be examined with the germanium detector, because the low efficiency of the detector resulted in inordinately long counting times. Two-exponential fits were made to all the concentration profiles from the niobium self-diffusion anneals. The diffusion coefficients of ^{95}Zr diffusing in niobium obtained from these fits were not well defined for every profile because the number of experimental points obtained in some of these tail regions was small.

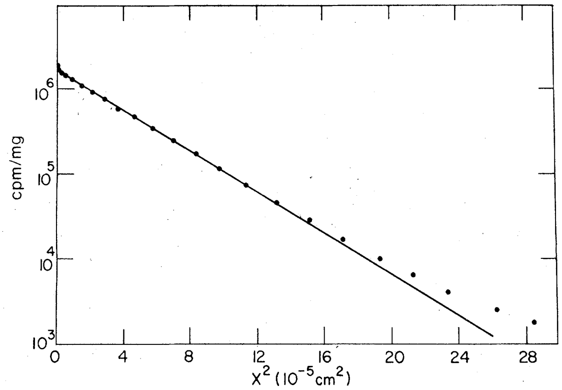

FIG. 1. Penetration plot for the diffusion of ^{95}Nb containing <1% ^{95}Zr. Tail appears at ~2 orders of magnitude of specific activity into sample. Anneal temperature is 2360 K.

In this work the accuracy of the diffusion coefficients for ^{95}Zr diffusing in niobium was improved by codiffusing a mixture of ^{95}Zr and ^{95}Nb. The 1:1 mixture, as purchased from the Oak Ridge National Laboratory, was diluted with the "pure" ^{95}Nb isotope to a ratio of ^{95}Zr to ^{95}Nb of approximately 0.35 for use in the diffusion anneals. This ratio, based on $D_{\text{Zr}} \sim 4\,D_{\text{Nb}}$, provided concentration profiles having significant regions where niobium and zirconium each dominated in activity. To obtain good counting statistics at low activity about 2.2 Mega-Bequerel (MBq) of isotope mixture were placed on each sample. This quantity amounts to less than a monolayer and does not violate the thin-film boundary conditions. The methods for sample annealing, sectioning, and counting were the same as those described in Ref. 5. A typical penetration profile is shown in Fig. 2.

Applied to measurements of isotope effects with the codeposition of two radioactive isotopes α and β, the thin-film serial sectioning technique has particular advantages. The relative concentrations of the two isotopes are given by Eq. (5). The masses of the isotopes are known exactly. To determine $f\Delta K$ to within 5% from Eq. (1), the quantity $D_\alpha/D_\beta - 1$ must be known to 5%. Combining Eqs. (1) and (5), one can estimate for the ^{90}Nb,

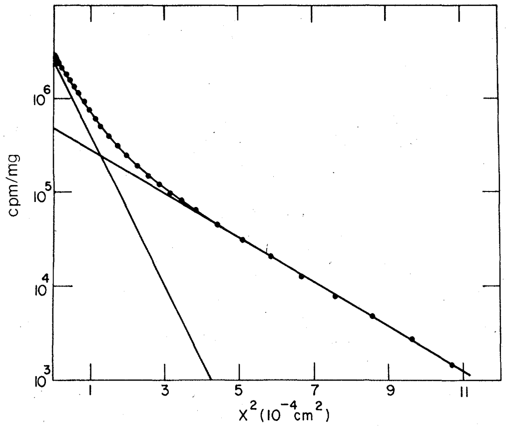

FIG. 2. Penetration plot for the codiffusion of ^{95}Zr-^{95}Nb. Straight lines are determined by the parameters of the best two-exponential fit, with the steeper line representing the ^{95}Nb self-diffusion and the lower slope line representing Zr diffusion in niobium. Anneal temperature is 2523 K.

^{95}Nb pair that $\ln(C_\alpha/C_\beta)$ changes by 7% if one takes sections into the crystal until the concentration of the diffusing species decreases three orders of magnitude. To know the slope of the isotope-effect plot to 5% means the ratio C_α/C_β must be known to 0.3%. This degree of accuracy can be achieved by careful counting, accumulating 10^6 counts for each section on a NaI(Tl) crystal and using either an energy or half-life discrimination method to determine C_α/C_β.

The improved energy discrimination available with a Ge(Li) detector as compared to a Na(Tl) detector would suggest[6] its use for measuring the ratio C_α/C_β. Each of the isotopes would have to be counted until 10^6 counts were accumulated. In Sec. I, where the count rate has decreased three orders of magnitude, the count rate on a NaI(Tl) (76 × 76-mm) well counter is about 33 cps. On a Ge(Li) detector with a volume of about 25 cm^3, this corresponds to approximately 1 cpm (within the peak, at approximately 0.75 MeV) and would require an inordinately long counting time. The efficiencies of counting with a Ge(Li) detector would have to be increased by three orders of magnitude to make the isotope-effect experiment feasible. The counting time could be reduced if the quantity of radioactive tracer was increased to about 0.7 Giga-Bequerel (GBq) (18.9 mCi). The thin-film condition (less than 0.1 $\sqrt{Dt}$) would be violated at such high activity levels, however, unless a carrier-free isotope was available. A sample containing an activity of about 0.7 GBq would also present safety problems for diffusion sectioning. In general, counting with a Ge(Li) detector is not suitable for measuring isotope effects in diffusion.

The ^{90}Nb isotope was produced by both of the reactions $^{89}Y(^3He, 2n)^{90}Nb$ and $^{89}Y(\alpha, 3n)^{90}Nb$ and subsequent chemical separation. Both reactions produced a significant amount of ^{89}Nb ($T_{1/2} = 1.9$ h) that decayed to ^{89}Zr. After cyclotron irradiation, the samples were stored for 32 h to permit all the ^{89}Nb to convert to ^{89}Zr before separation. The state of the art for Nb-Zr separation prior to this work was about 0.1-at.% Zr.[7,8] The overlap of the γ spectra of Nb and Zr (either the ^{95}Nb-^{95}Zr or the ^{90}Nb-^{89}Zr pair) limited our minimum detectable levels of Zr to about 150 at.ppm with a 13-h count and using a Ge(Li) detector (volume is 25 cm^3, resolution is 1.9 kV at 1.33-MeV ^{60}Co, and peak to Compton ratio of 25). For the short-half-life pair ^{90}Nb-^{89}Zr, lower concentrations can be measured by waiting for the Zr concentration to increase relative to that of the Nb and either using a Ge(Li) counter for energy discrimination of the two species or measuring the decay of a ^{90}Nb sample using a NaI(Tl) counter. The decay of a ^{90}Nb sample was measured since this method also allowed the half-life of ^{90}Nb to be determined. Three-exponential fits to the decay profiles for our best chemical separation, counted for 280 h on a NaI well counter, indicated about 100 at.ppm ^{89}Zr and 15 at.ppm ^{95}Nb. Previous determinations of the ^{90}Nb half-life followed the decay over only eight half-lives and did not account for small amounts of ^{89}Zr impurity. Only after eight half-lives will the curvature due to the ^{89}Zr be detectable. When the ^{89}Zr was taken into account and a two-exponential fit was made to the half-life data, the ^{90}Nb half-life was determined to be 14.5 h, or 1% lower than previously reported.[7,8]

III. EXPERIMENTAL RESULTS

The diffusion rates of ^{95}Zr and ^{95}Nb, assuming a bulk diffusion process for both, were obtained by fitting the penetration profiles to Eq. (4). This procedure is valid only if the isotopes decay independently and no daughter products are involved. At a time $t = 0$ (i.e., at the end of the diffusion anneal), the individual count rates are given by

$$C_{Nb}(x,0) = C_{Nb}(0,0)\exp(-Bx^2) \tag{6a}$$

and

$$C_{Zr}(x,0) = C_{Zr}(0,0)\exp(-Hx^2)\ . \tag{6b}$$

At a time t after the anneal (the time that the sections are counted) and for any section in the sample, the count rate of the zirconium $C_{Zr}(x,t)$ and of the niobium $C_{Nb}(x,t)$ are given by the equations

$$C_{Nb}(x,t) = \frac{\lambda_2}{\lambda_2 - \lambda_1}\, C_{Zr}(x,0)(e^{-\lambda_1 t} - e^{-\lambda_2 t}) + C_{Nb}(x,0)\exp(-\lambda_2 t) \tag{7a}$$

and

$$C_{\mathrm{Zr}}(x,t)=C_{\mathrm{Zr}}(x,0)\exp(-\lambda_1 t)\ , \tag{7b}$$

where λ_1 and λ_2 are the decay constants of zirconium and niobium, respectively, and $C(x,0)$ is the count rate at time $t=0$ and position x.

The total measured count rate using a NaI(Tl) detector is the sum of Eqs. (7a) and (7b). The terms of Eq. (4) can, from the equations above, be identified as

$$A=C_{\mathrm{Nb}}(0,0)\exp(-\lambda_2 t)\ ,$$

$$G=C_{\mathrm{Zr}}(0,0)\left(\frac{\lambda_2}{\lambda_2-\lambda_1}\left(e^{-\lambda_1 t}-e^{-\lambda_2 t}\right)+e^{-\lambda_1 t}\right) \tag{8}$$

$$B=(4D_{\mathrm{Nb}}t_A)^{-1}\ ,$$

and

$$H=(4D_{\mathrm{Zr}}t_A)^{-1}\ ,$$

where t_A is the anneal time. The relationships given in Eq. (8) permit the calculation of the correct concentrations of niobium and zirconium at time $t=0$.

On one sample, the first 20 sections (each about $0.2\sqrt{Dt}$ thick) were analyzed using a Ge(Li) detector to determine the ratio of niobium activity to zirconium activity. Sections deeper than $4\sqrt{Dt}$ could not be analyzed, because the counting times were too long. Equation (7) allowed correcting of the ratios back in time to $t=0$. The values of $C_{\mathrm{Nb}}(x,0)/C_{\mathrm{Zr}}(x,0)$ obtained from the Ge(Li) detector and from the NaI(Tl) detector agreed within 1%.

The values of the diffusion coefficients obtained from the fits of data to Eq. (3) are listed in Table I and plotted in Fig. 3. Two values are given for each temperature. The temperature was measured by an optical pyrometer sighted on a blackbody cavity formed by the faces of two diffusion samples, one above the other.[5] As a result of the gradients in the electron-beam furnace, the upper sample was cooler than the lower sample. The pyrometer read an average temperature for the two sample faces. Values of ^{95}Zr diffusion in niobium obtained from the tails of the previous measurements of self-diffusion of pure niobium are also shown in Fig. 3. A least-squares fit to the diffusion coefficients determined in this work and the diffusion coefficient from the tails[5] gives the Arrhenius relation

$$D=0.85\exp(-3.93eV/kT)\,\mathrm{cm^2\,sec^{-1}}\ . \tag{9}$$

This is in reasonable agreement with earlier measurements[9] of zirconium diffusion in niobium obtained using an electron microprobe.

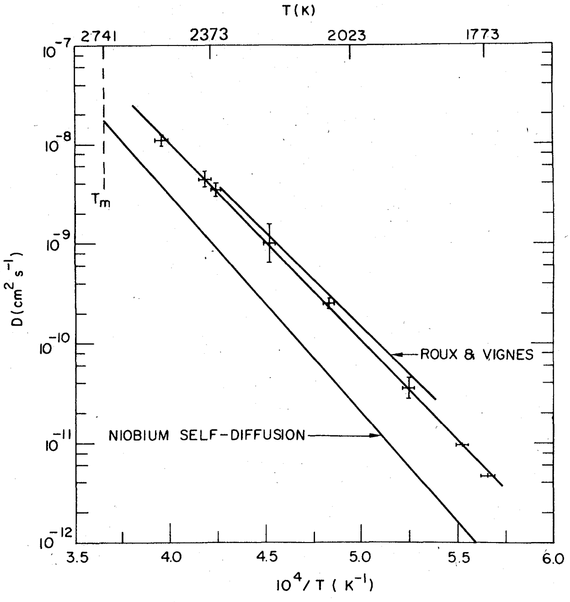

FIG. 3. Arrhenius plot of Zr diffusion in Nb and Nb diffusion in Nb obtained from codiffusing ^{95}Zr-^{95}Nb. Also shown are D_{Zr} (Nb) from the "tail" data, Vignes (Ref. 9) heterodiffusion data and diffusion data for "pure" niobium from Ref. 5.

IV. DISCUSSION

The effect of fast-diffusing zirconium on the accuracy of the measurements of niobium self-diffusion is greater at lower temperatures. To study

TABLE I. Diffusion coefficients from ^{95}Nb-^{95}Zr codiffusion.

Temperature (K)	Anneal time (10^3 sec)	D_{Nb} (cm^2 sec^{-1})	D_{Zr} (cm^2 sec^{-1})	$D_{\mathrm{Zr}}/D_{\mathrm{Nb}}$
2523	2.9	$(3.79\pm0.04)\times10^{-9}$	$(1.25\pm0.01)\times10^{-8}$	3.30 ± 0.06
2523	2.9	$(2.60\pm0.10)\times10^{-9}$	$(9.58\pm0.01)\times10^{-9}$	3.68 ± 0.15
2391	2.9	$(1.38\pm0.02)\times10^{-9}$	$(5.41\pm0.03)\times10^{-9}$	3.92 ± 0.08
2391	2.9	$(9.04\pm0.14)\times10^{-10}$	$(3.68\pm0.03)\times10^{-9}$	4.07 ± 0.10
2068	81.0	$(5.49\pm0.12)\times10^{-11}$	$(2.89\pm0.02)\times10^{-10}$	5.26 ± 0.16
2068	81.0	$(4.35\pm0.08)\times10^{-11}$	$(2.23\pm0.02)\times10^{-10}$	5.12 ± 0.15
1900	81.0	$(8.79\pm0.40)\times10^{-12}$	$(4.51\pm0.15)\times10^{-11}$	5.13 ± 0.40
1900	81.0	$(6.53\pm0.10)\times10^{-12}$	$(3.82\pm0.03)\times10^{-11}$	5.85 ± 0.14

any low-temperature (less than 1273 K) self-diffusion phenomena in niobium such as the effects of oxygen or radiation-enhanced diffusion, the amount of ^{95}Zr in the ^{95}Nb isotope purchased from the Oak Ridge National Laboratory would need to be reduced before reliable data could be obtained.

The effect of the zirconium impurity in the atomic ppm range can render isotope-effect measurements for niobium self-diffusion meaningless. The half-life separation technique follows the total activity C_{tot} for each section as a function of time, i.e.,

$$C_{\text{tot}} = C_A \exp(-\lambda_A t) + C_B \exp(-\lambda_B t) \ . \tag{10}$$

An accurate value of C_A and C_B can be determined by a two-exponential fit of the data if accurate values of the decay constants λ_A and λ_B are known. However, the niobium isotopes ^{95}Nb($T_{1/2} = 35$ day) and ^{90}Nb($T_{1/2} = 15$ h) contain small amounts of ^{95}Zr($T_{1/2} = 65$ day) and ^{89}Zr($T_{1/2} = 78$ h), respectively. These isotopes will be referred to as α, β, Δ, and ϕ, respectively. In principle, a four-exponential fit of the data could be made, but the half-lives of the four isotopes are not sufficiently different. If the levels of the radioactive impurities had been smaller and undetected, a two-exponential fit would have been made.

The following analysis shows the danger of fast-diffusing ultralow-level radioactive impurities. The two-exponential fitting routine would associate the activity into two groups: short-lived and long-lived isotopes. We have simulated this effect by letting $C_A = C_\alpha + C_\Delta$ and $C_B = C_\beta + C_\phi$. Each isotope will obey its own Gaussian depth dependence, i.e.,

$$C_\alpha = C_\alpha^0 \exp(-x^2/4D_\alpha t) \ . \tag{11}$$

The initial concentrations are related by $C_\Delta^0 = \gamma C_\alpha^0$ and $C_\phi^0 = Z C_\beta^0$. The diffusion coefficients are related by $D_\Delta = \delta D_\beta$ and $D_\phi = \delta D_\alpha$. The quantity of interest $\ln(C_A/C_B)$ is given by

$$\begin{aligned}\ln\left(\frac{C_A}{C_B}\right) &= \ln\left(\frac{C_\beta^0}{C_\alpha^0}\right) + \ln\left(\frac{C_\alpha}{C_\alpha^0}\right)\left[\left(\frac{D_\alpha}{D_\beta}\right) - 1\right] \\ &= \ln\left\{1 + \gamma \exp\left[\frac{D_\alpha}{D_\beta}\left(\frac{1-\delta}{\delta}\right)\ln\left(\frac{C_\alpha}{C_\alpha^0}\right)\right]\right\} \\ &\quad - \ln\left[1 + Z \exp\left(\frac{\lambda(1-\delta)}{\delta}\right)\right] \ .\end{aligned} \tag{12}$$

Equation (12) is plotted in Fig. 4 for $D_\alpha/D_\beta = 1.01$, $\delta = 4$ (values appropriate for the present niobium work) and various values of γ and Z. The magnitude of the value of $(D_\alpha/D_\beta - 1)$ would not be significantly different for isotope-effect measurements on other metals.

For the case of no isotopic contamination ($\gamma = Z = 0$), Eq. (12) reduces to Eq. (5). Figure 4 shows clearly that small concentrations of either the short- or long-lived impurities have drastic effects on the slope of $\ln(C_A/C_B)$. The concentrations used in Fig. 4 are of the same order as the lowest zirconium concentrations obtained in the niobium isotope that had been chemically separated by the Analytical Chemical Group at Argonne National Laboratory. It is interesting to note that a small quantity of fast-diffusing impurity ($\gamma = 10^{-3}$) would not produce a tail in the penetration profile, but the effect it would have on the $\ln(C_A/C_B)$ vs $\ln C_A$ plot is considerable. Figure 4 also shows that if both short- and long-lived impurities were present in similar concentrations, the effect on the slope would be small.

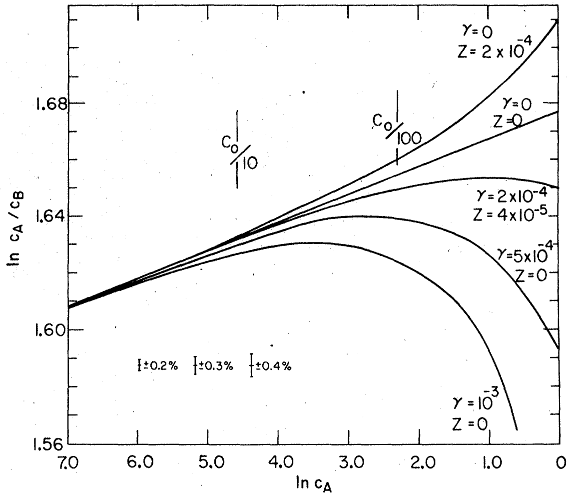

FIG. 4. A $\ln C_A/C_B$ vs $\ln C_A$ isotope-effect plot indicating the deviation obtained from the expected straight line ($\gamma = Z = 0$) for various impurity levels of ^{89}Zr and ^{95}Zr. $E = (D_\alpha/D_\beta) - 1 = 0.01$; $\delta = 4.5$. The error bars at the lower left of the diagram represent various error levels in $\ln(C_A/C_B)$.

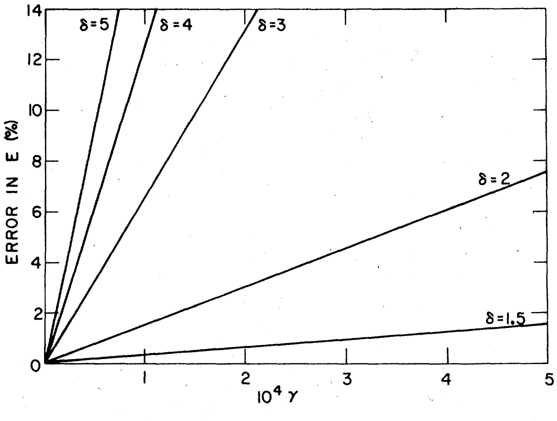

FIG. 5. Error in the isotope effect for various levels (γ) of fast-diffusing ($\delta > 1$) impurity isotopes if the sample is sectioned until the count rate decreases three orders of magnitude from its initial value.

Differentiation of Eq. (12) allows the calculation of the error in the slope, and therefore $(D_\alpha/D_\beta - 1)$ for various values of γ, Z, and δ. Figure 5 shows the percentage error in $\dot{E} = (D_\alpha/D_\beta - 1)$ calculated for $E = 0.01$, $Z = 0$, and a profile extending $5.25\sqrt{Dt}$ into the sample. To determine the isotope effect to ± 5%, niobium isotopes with less than 50 at.ppm zirconium would be needed. This level of impurity was below the level of detection of the Ge(Li) detector. Only once was the chemically separated niobium isotope we received well below the detection limit. The error caused by the fast-diffusing impurity can be reduced by examining the profile over a smaller depth, but the effect of experimental scatter of the individual values of $\ln(C_A/C_B)$ will tend to nullify any gain found by examining shallower profiles. Figure 5 also shows the accuracy with which the impurity level and ratio of diffusion coefficients must be known if the effects of fast-diffusing impurities are to be corrected.

The present measurements have determined the ratio of the diffusion coefficients with sufficient accuracy to correct for the presence of zirconium had niobium isotope-effect measurements been made. Unfortunately, the amount of zirconium isotope present, which also must be known for making such measurements, cannot be determined with sufficient accuracy. The concentration ratio of Zr to Nb can be determined for both ^{95}Nb and ^{90}Nb isotopes prior to the diffusion anneal. However, it was was found experimentally that the concentration ratios changed in an irreproducible manner and a straight $(D_{\mathrm{Zr}}/D_{\mathrm{Nb}})^{1/2}$ correction did not lead to the correct values of zirconium concentrations. The inability to purify the niobium or correct for the presence of the zirconium prevented the measurements of the isotope effect in niobium self-diffusion.

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