Fast diffusion of ^{59}Fe in β-Zr and β-Zr-Fe alloys

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Abstract. The fast impurity diffusion of ^{59}Fe in β-Zr and β-Zr–Fe alloys was investigated. Complementary information about the possible diffusion mechanism was achieved by examining the influence of Fe addition on the Zr self-diffusion (enhancement factor b). Further evidence on the diffusion process in detail was evaluated comparing the macroscopic tracer measurements with microscopic experiments where jump frequencies of the diffusing Fe atoms were studied by quasielastic Mößbauer spectroscopy. The overall mass transport of Fe in β-Zr as observed by tracer measurements can be entirely explained by a dissociative diffusion mechanism. The diffusional line broadening observed by Mößbauer spectroscopy originates from diffusion via regular lattice sites (vacancy mechanism) where most of the Fe atoms are dissolved.

1. Introduction

The phenomenon of fast diffusing metallic solutes remains an interesting subject in diffusion research. The increasing variety of systems in which anomalous fast impurity diffusion has been observed has not lead to a detailed uniform picture of the diffusion mechanism [1]. A further approach to obtain information about the atomic jump process will be made by comparing quasielastic Mößbauer spectroscopy (QMS) experiments [2] and tracer diffusion studies, which will be reported here.

Nuclear methods like QMS or quasielastic neutron scattering (QNS) can yield information about the jump frequencies of atomic migration and about the jump vector if single crystals are examined. However these so-called microscopic methods are restricted to various experimental conditions, which considerably limit the number of systems to be studied [3].

Most investigations on anomalous fast impurity diffusion were performed on lead-based systems. A common feature of the fast diffusing metallic solutes in these systems is their small solubility, which is generally of the order of several hundred ppm. This hinders a sufficient accuracy of nuclear methods that study the low concentration defect itself [4,5]. A more successful approach was achieved by studying the lattice response of the disturbed matrix by the dissolution of the fast diffusing impurities [6]. From these studies it can be summarized that the fast diffusing solutes are partially dissolved on substitutional sites and that a small fraction diffuses via an interstitial type mechanism. In a more recent study on fast diffusion of Co in Nb with the

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radiotracer technique two-stage diffusion profiles were observed [7] leading to a similar interpretation on fast impurity diffusion.

A suitable system to combine microscopic and macroscopic diffusion studies is the Zr–Fe system for the following reasons.

(i) The solubility range of Fe in β-Zr is in the order of several at.% [8] which enables the QMS to obtain reliable count rates.

(ii) [57]Fe is the common Mößbauer isotope and technical problems such as high-temperature Mößbauer spectroscopy could be managed [9].

(iii) The diffusion of Fe in β-Zr is sufficiently high to be observed within the time window of QMS.

(iv) No significant problems arise handling the radioisotopes ^{59}Fe and [95]Zr used in this study.

In this paper we report on tracer diffusion experiments of ^{59}Fe in β-Zr and β-Zr–Fe alloys with 0.5, 2.0 and 3.5 at.% Fe, and on the investigation of the enhancement factor b for the [95]Zr diffusion in β-Zr–Fe alloys at 1221 K. To perform a quantitative comparison of QMS results and tracer measurements a re-examination of the diffusion of ^{59}Fe in β-Zr seemed to be unalterable due to the large discrepancies of the diffusion results reported in literature [10, 11].

2. Experimental procedure

The radiotracer technique combined with a serial sectioning procedure was applied to determine the diffusion coefficients. The concentration $c(x,t)$ of the radioactive tracer, that has diffused from a thin layer deposited on the surface of the sample to a penetration depth x during an anneal time t is given by the solution of Fick's second law:

$$c(x,t) = \frac{c_0}{\sqrt{\pi D^* t}} \exp\left(-\frac{x^2}{4 D^* t}\right) \tag{1}$$

where c_0 is the tracer concentration at $x = 0$ and $t = 0$ and D^* is the tracer diffusion coefficient.

This joint study of QMS and tracer measurements was performed using identically prepared starting material to exclude spurious sample related effects. For the diffusion experiments in pure β-Zr as well as for the alloy preparation high-purity Zr material delivered by Teledyne Wah Chang was used. In addition the diffusion of ^{59}Fe was measured using Zr of even lower impurity content delivered from Materials Research Company in MARZ-grade quality (for the impurity contents see [12]). The alloy preparation was done by levitation melting and is described in detail elsewhere [13]. The iron content of the alloy samples was analyzed by electron microprobe and agreed well with the nominal values. Cylindrical rods were cut by spark erosion and machined out to samples of diameter 8–10 mm and height 3–5 mm from the as melted alloy pellets. After polishing, etching and cleaning the samples were preannealed in a UHV chamber ($p \leq 5 \times 10^{-7}$Pa) to stabilize them in view of recrystallization and grain growth and to prevent spurious effects related to the martensitic phase transition. Due to the cycling through the β–α phase transition the surface of the samples had to be polished again. The ^{59}Fe tracer was deposited from a 0.5N HCl solution and dried on air. To reduce tracer evaporation during the diffusion anneal the samples were covered by a lid of pure Zr.

The heating of the samples was achieved in different ways depending on the temperature range required. For temperatures below 1300 K the samples were annealed in a quartz tube by a tube furnace. The quartz tube was flanged to a turbo pump allowing a vacuum of $p \leq 10^{-6}$Pa and temperature measurements of the samples by a calibrated Ni–NiCr thermocouple accurate to ± 1 K. In the temperature range from 1300–1650 K the sample heating was achieved by a specially designed tantalum furnace which was mounted in a UHV chamber ($p \leq 5 \times 10^{-7}$Pa) [14]. The temperature was measured by a micro-pyrometer with an accuracy of ± 8 K. For temperatures above 1650 K the sample was mounted in a molybdenum box and heating was achieved by electron bombardment. The diffusion anneal took place in the same UHV chamber as mentioned before and temperature was controlled by a two-colour pyrometer with an accuracy of ± 10 K.

After the diffusion anneal the samples were reduced in diameter to prevent the influence of surface diffusion and were sectioned by lathe. The sections were weighted and dissolved in acid to achieve a homogeneous counting geometry in a well-type NaJ detector.

The measurement of the enhancement factor b was taken in a manner similar to that mentioned above. The ^{95}Zr tracer in equilibrium with its daughter nuclide ^{95}Nb was deposited from an oxalic acid solution onto the polished surface. The diffusion anneal of six samples with different Fe content was performed simultaneously in a specially designed tube furnace that allowed a homogeneous temperature distribution within ± 0.5 K. The identical anneal conditions increase the relative accuracy of the diffusion coefficients. Counting the activity of the sections was done in a well-type Ge detector that permitted the separation of the ^{95}Zr and ^{95}Nb decays.

3. Results

The high diffusivity and the corresponding short anneal times in the electron heating system limited the extension in the high-temperature regime. Some typical examples of the obtained penetration profiles are shown in figure 1. In the investigated temperature range (1172 K to 1886 K) the calculated diffusion coefficients of ^{59}Fe in pure β-Zr can be represented by the following Arrhenius relation:

$$D_{\text{Fe}}^{*}(T) = 5.3(3) \times 10^{-7} \exp\left(-\frac{1.08(4)\text{eV}}{k_{\text{B}}T}\right) \text{ m}^2\text{s}^{-1}. \tag{2}$$

The results are summarized in table 1 and are plotted in Arrhenius form in figure 2 together with the data reported in literature by Pavlinov [10] and Patil *et al* [11]. The small scatter of the present data around the least squares fit mainly results from the different accuracy attainable in temperature measurement and anneal time corrections as described above. No significant influence of the purity of the different Zr materials used was observed.

There is good agreement between the present results and those of Pavlinov [10] while the data reported by Patil [11] are considerably smaller. This discrepancy remains inexplicable, especially if we consider the results we obtained for the ^{59}Fe diffusion in the different Zr–Fe alloys. The results are summarized in table 1. The Arrhenius plot of these data (figure 3) shows that the ^{59}Fe-tracer diffusion is almost independent from the iron content of the Zr matrix.
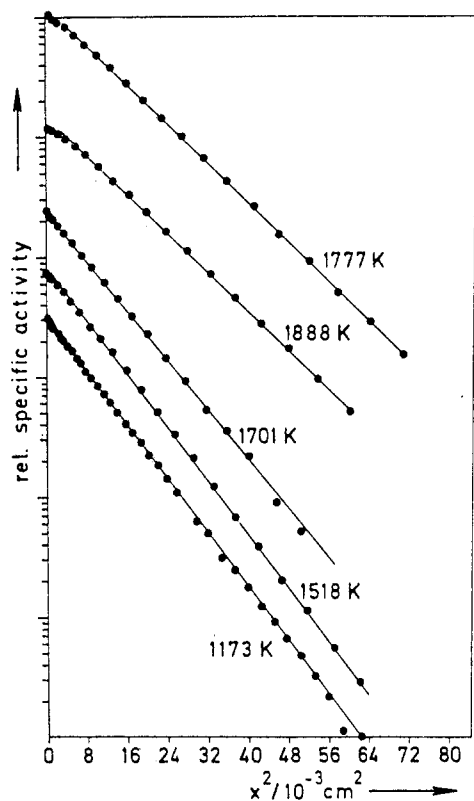
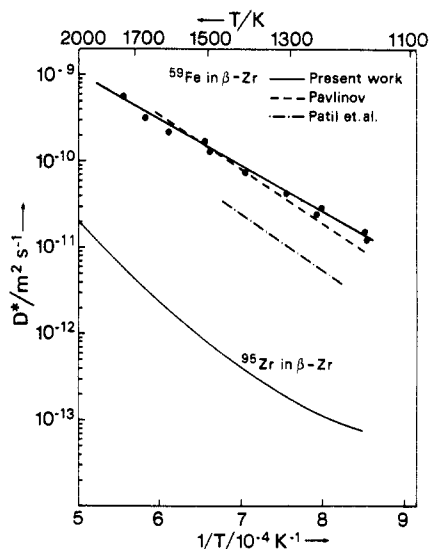**Figure 1.** Typical penetration profiles of ^{59}Fe in β-Zr for different temperatures.

Figure 2. Arrhenius plot of ^{59}Fe diffusion in β-Zr in comparison with Zr self-diffusion [14] including Fe diffusion data from the literature [10, 11].

Due to the short diffusion anneal times in the β phase one might speculate that Fe-rich precipitations which had been formed in the α phase were not able to re-dissolve completely leading to non-equilibrium conditions. To study this possible influence an alloy sample with 3.5 at.% Fe was pre-annealed in the β phase at $T = 1346$ K for about 4 hours before the ^{59}Fe-tracer was deposited *in situ* during the anneal. The evaluated diffusion coefficient agrees, within the experimental error, with the results obtained as described above.

Taking the scatter of the ^{59}Fe diffusion coefficients as a measure of the experimental uncertainty of the present investigation it seems to be allowed to characterize all presently measured ^{59}Fe diffusion coefficients by the same Arrhenius relation :

$$D^{*}_{Fe}(T) = 7.3(3) \times 10^{-7} \exp\left(-\frac{1.12(2)\text{eV}}{k_{\text{B}}T}\right) \text{ m}^2\text{s}^{-1}. \tag{3}$$

This situation, however, is different for the diffusion of the Zr matrix component. Figure 4 shows diffusion profiles of ^{95}Zr in Zr–Fe alloys. Again the decay in counting rates could be followed over more than three decades, indicating perfect Gaussian behaviour. Table 2 gives the calculated Zr diffusion coefficients. The observed linear

Table 1. Diffusion coefficients of ^{59}Fe in β-Zr and β-Zr–Fe alloys

Temperature [K]	Anneal time [s]	Diffusion coefficient $[\mathrm{m^2 s^{-1}}]$	c [at.% Fe]
1886	363	$7.40(35) \times 10^{-10}$	0.0
1777	465	$5.72(27) \times 10^{-10}$	0.0
1701	693	$3.04(14) \times 10^{-10}$	0.0
1615	855	$2.05(10) \times 10^{-10}$	0.0
1518	1127	$1.72(9) \ \ \times 10^{-10}$	0.0
1493	897	$1.30(9) \ \ \times 10^{-10}$	0.0
1410	1507	$7.37(19) \times 10^{-11}$	0.0
1320	2401	$4.23(12) \times 10^{-11}$	0.0
1272	7157	$2.34(7) \ \ \times 10^{-11}$	0.0
1253	5406	$2.88(8) \ \ \times 10^{-11}$	0.0
1173	4835	$1.54(9) \ \ \times 10^{-11}$	0.0
1172	16106	$1.20(7) \ \ \times 10^{-11}$	0.0
1575	1142	$1.67(8) \ \ \times 10^{-10}$	0.5
1410	1705	$5.33(21) \times 10^{-11}$	0.5
1184	6923	$1.39(3) \ \ \times 10^{-11}$	0.5
1173	16106	$1.04(2) \ \ \times 10^{-11}$	0.5
1151	10040	$1.04(3) \ \ \times 10^{-11}$	0.5
1123	7097	$7.00(13) \times 10^{-12}$	0.5
1581	684	$1.71(11) \times 10^{-10}$	2.0
1432	1138	$6.09(20) \times 10^{-11}$	2.0
1246	3557	$1.74(7) \ \ \times 10^{-11}$	2.0
1203	72057	$1.61(5) \ \ \times 10^{-11}$	2.0
1154	10601	$1.05(6) \ \ \times 10^{-11}$	2.0
1123	3771	$5.54(15) \times 10^{-12}$	2.0
1589	710	$2.45(10) \times 10^{-10}$	3.5
1370	1845	$5.50(18) \times 10^{-11}$	3.5
1346	2714	$3.49(10) \times 10^{-11}$	3.5
1231	4112	$2.12(9) \ \ \times 10^{-11}$	3.5
1171	7809	$9.72(18) \times 10^{-12}$	3.5
1123	7106	$7.12(13) \times 10^{-12}$	3.5
1078	3706	$3.41(7) \ \ \times 10^{-12}$	3.5

increase of the Zr diffusivity with increasing iron content up to 1.8 at.% Fe, as shown in figure 5, can be described by the relation

$$D^*_{\mathrm{Zr}}(c_{\mathrm{Fe}}) = D^*_{Zr}(0)(1 + bc_{\mathrm{Fe}}) \tag{4}$$

which defines the linear enhancement factor of self-diffusion. The present investigation yields $b = 47(3)$.

Table 2. Diffusion coefficients of ^{95}Zr in β-Zr and β-Zr–Fe alloys.

Temperature [K]	Anneal time [s]	$D^*[10^{-13}\mathrm{m^2 s^{-1}}]$	c [at.% Fe]
1221	73490	1.07(2)	0.0
1221	73490	1.24(2)	0.3
1221	73490	1.42(3)	0.5
1221	73490	1.63(3)	1.0
1221	73490	1.99(4)	1.8
1221	73490	3.17(6)	3.5

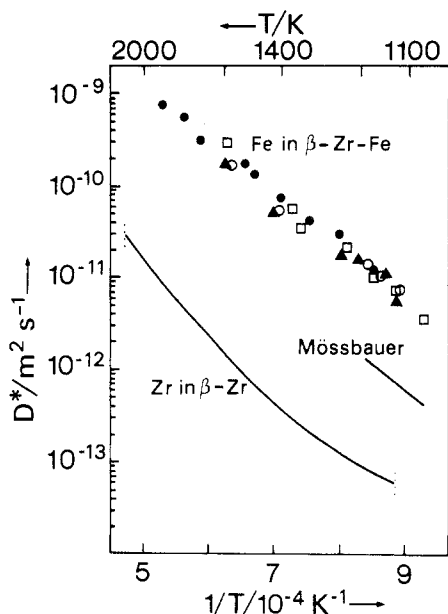**Figure 3.** Arrhenius plot of ^{59}Fe in β-Zr ($\bullet$) and β-Zr–Fe alloys with 0.5 (o), 2.0 ($\blacktriangle$) and 3.5at.% Fe ($\square$) in comparison with diffusion data obtained by Mößbauer measurements (QMS) [2].

4. Discussion

The very large diffusion coefficients of Fe in β-Zr, the activation enthalpy Q and the small frequency factor D_0 correspond to the typical characteristics of metallic fast diffusers as observed, for example, in Pb. These features and the measured small enhancement factor of the Zr self-diffusion b as well as the almost non-existing influence of the iron content on the Fe impurity diffusion favour an interstitial-type diffusion mechanism. The striking result of our joint study is the large difference of diffusivities observed by tracer and QMS measurements. A similar observation had been made by studying the diffusion of Fe in β–Ti by QMS [15]. Whereas the tracer diffusion experiments yield diffusion coefficients (D_{Fe}^*) that are more than two orders of magnitude higher than self-diffusion in β-Zr [14] the QMS studies lead to diffusivities (D_{Fe}^{QMS}) that are ten times slower than D_{Fe}^* (figure 3). For the observed Fe tracer diffusion data a vacancy mechanism can be excluded for the following reason: the high ratio of D_{Fe}^*/D_{Zr}^* should lead to a strong enhancement of the Zr self-diffusion with increasing iron content of the host matrix. There exists a minimum enhancement factor b^{min} calculated with the widely used jump-frequency model [16] for which a given ratio of D_{Fe}^*/D_{Zr}^* is compatible with a monovacancy mechanism (table 3).

Furthermore the evaluated diffusion data give no hint that an interstitial-vacancy pair (IV pair) mechanism, as discussed in the literature [17], is responsible for the fast
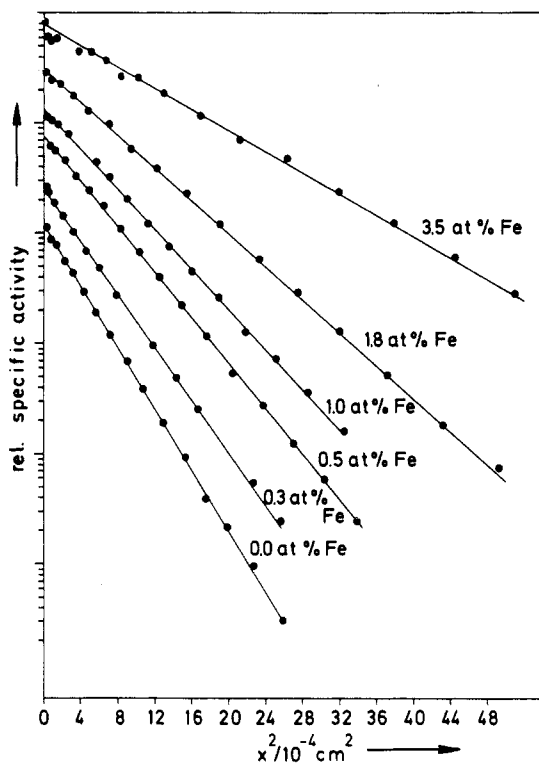
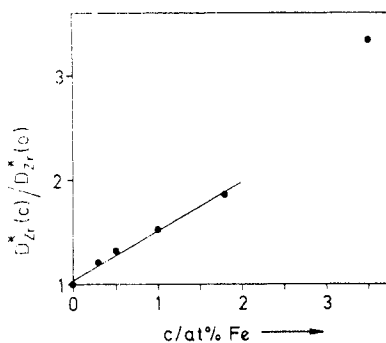**Figure 4.** Penetration profiles of ^{95}Zr diffusion in β-Zr and β-Zr–Fe alloys at 1221 K.

Figure 5. Concentration dependence of the ^{95}Zr diffusion in β-Zr on the iron content of the matrix normalized to the ^{95}Zr diffusion in pure β-Zr . The linear increase determines the enhancement factor b.

Table 3. Calculation of enhancement factors for D^*_{Zr} in β-Zr–Fe alloys.

	T [K]	D_{Fe}/D^*_{Zr}	b^{exp}	b^{min} [16]	b^{IVpair} [17]
Fe (tracer)	1221	159	47	319	173
Fe (QMS)	1221	16	47	39	17

iron diffusion (table 3).

Using the QMS data to calculate via $D_{\text{Fe}}^{\text{QMS}}/D_{\text{Zr}}^* = 16$ ($T = 1221$ K) the minimum enhancement factor, which is compatible with a vacancy mechanism [16], we obtain $b^{\text{min}} = 39$. Compared with the experimental b value, $b^{\text{exp}} = 47$, the QMS data can fully be explained to measure Fe diffusion jumps via a vacancy diffusion mechanism. This leads us to the conclusion that the diffusion of Fe in β-Zr takes place via two different mechanisms. With the special capability of QMS to determine the jump frequency of the diffusing atoms directly, the Fe diffusion via substitutional sites could be evaluated. Discussing QMS data alone, such a conclusion remains speculative in the way that for the conversion of observed jump frequencies in diffusion coefficients the jump length has to be known. Only QMS experiments on single crystals could clarify the situation. The occurrence of the β–α phase transition in the Zr–Fe system, however, makes such experiments difficult.

Besides the vacancy mechanism there must exist a second type of jump frequencies or mechanism, the sum of which is detected with the tracer measurements. The macroscopic mass transport can be described as the sum of the fluxes via the two (or more) diffusion mechanisms. Assuming that the QMS experiments detect a vacancy mechanism we propose, due to the high diffusivity of the Fe atoms, an interstitial-type mechanism for the second one:

$$j^* = j^{\text{QMS}} + j^i. \tag{5}$$

There must exist a continuous exchange of Fe atoms placed either on substitutional (Fe^s) or interstitial (Fe^i) sites including a vacancy (V):

$$\text{Fe}^i + \text{V} \rightleftarrows \text{Fe}^s. \tag{6}$$

If this exchange does not lead to a macroscopic flux of Fe atoms ($j^{\rightleftarrows} = 0$) equation (5) can be rewritten with Fick's first law :

$$j = -D\frac{\partial c}{\partial x} \tag{7}$$

in the form

$$D^* = D^{\text{QMS}}\frac{c^{\text{QMS}}}{c} + D^i\frac{c^i}{c} \tag{8}$$

with $c = c^{\text{QMS}} + c^i$ the overall impurity content of the host matrix.

In the same way as in the tracer measurements no distinct dependence of the Fe diffusivity was observed in the QMS investigations. As the QMS technique detects jumps of iron atoms via monovacancies, an enhancement of D^{QMS} with increasing Fe concentration would have been expected. Assuming, as was often observed in other systems, a similar enhancement factor for impurity as for self-diffusion, such a relatively small change in D^{QMS} is beyond the accuracy of this microscopic technique. Furthermore, this enhanced Fe diffusion via vacancies results in an increase of the total flux of Fe atoms. However, due to the difference of more than one order of magnitude between D^{QMS} and D^* this enhancement of D^{QMS} is small compared with the total flux of Fe atoms and is therefore too insignificant to be detected in our tracer study.

Nothing can be said so far about the fractions of substitutionally or interstitially dissolved Fe. However, it seems to be reasonable to postulate that most of the dissolved Fe is placed on substitutional sites. One of the most fruitful results of our joint

study on fast impurity diffusion is to determine the total macroscopic diffusivity D^* of Fe in β-Zr as well as the partial diffusivity via the vacancy mechanism. This enables us to correlate via equation (8) the diffusivity of the interstitial-type diffusion mechanism with the fraction of interstitially dissolved Fe atoms, e.g. at 1221 K (figure 6). Estimating an upper limit for the interstitial mobility, e.g. the diffusivities observed in liquids ($D \approx 10^{-9}\,\text{m}^2\,\text{s}^{-1}$) the fraction of interstitially dissolved iron atoms is of the order of 1% of the overall iron content of the β-Zr matrix. This fraction would be too small to be detected by the QMS measurements.
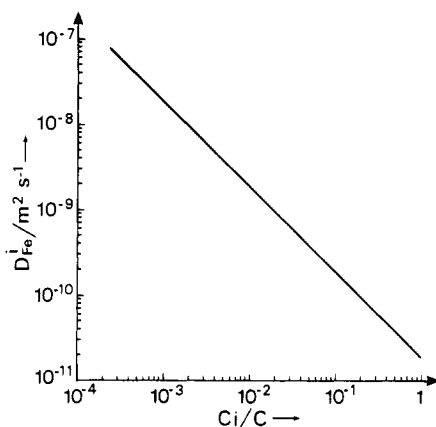

Figure 6. Diffusivity D^i_{Fe} of the interstitial component versus the ratio of interstitial solubility c^i to the overall iron content c at 1221 K.

The detailed diffusion mechanism of the fast interstitial component still remains speculative. However, it seems worthwhile to discuss a mechanism more complicated than a simple interstitial mechanism with jumps occuring between tetrahedral or octahedral sites respectively. This mechanism has to explain two features of fast impurity diffusion.

(i) The high mobility of Fe atoms, which is even higher than that of interstitially dissolved gaseous impurities like oxygen or nitrogen in β-Zr [19].

(ii) The significantly small isotope effect ($E \approx 0.25$) as observed, e.g., for Co in β-Zr [18] and in various lead-based systems [1].

To our knowledge the most convenient mechanism discussed in the literature is the so-called impurity-host diplon mechanism. For a detailed description of this mechanism we refer to some review articles [1]. The unique feature of this mechanism is to involve host atoms in the diffusion jump, which leads to a small isotope effect without accelerating the host diffusivity, which would be in contradiction to the observed small enhancement factor b.

5. Summary

The anomalous fast Fe diffusion in β-Zr has been studied over the whole temperature range of the β-phase by tracer diffusion experiments. Additional information about the diffusion mechanism was evaluated by studying the influence of Fe additions to the Zr matrix on the ^{59}Fe as well as the ^{95}Zr self-diffusion. Comparing these macroscopic

measurements with microscopic QMS experiments we conclude that the Fe diffusion in β-Zr occurs via a substitutional-interstitial exchange mechanism. Whereas the QMS studies detect the diffusion of substitutionally dissolved Fe atoms via vacancies, the tracer measurements examine the total flux of all Fe atoms, which is dominated by a very fast interstitial component.

Acknowledgments

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