# Pressure dependence of self- and solute diffusion in bcc zirconium

P. Knorr

Institut für Metallforschung, Universität Münster, Wilhelm-Klemm-Strasse 10, D-48149 Münster, Germany

J. Jun and W. Lojkowski

High Pressure Research Center, Polish Academy of Sciences, Sokolowska 29, P-01142 Warszawa, Poland

### Chr. Herzig

## Institut für Metallforschung, Universität Münster, Wilhelm-Klemm-Strasse 10, D-48149 Münster, Germany (Received 28 July 1997)

The pressure effect of self-diffusion in the high-temperature bcc phase of zirconium has been studied with high accuracy using the radiotracer technique. Activation volumes of  $0.184\pm0.016\Omega$  ( $\Omega$ : atomic volume) at 1423 K and  $0.213\pm0.014\Omega$  at 1273 K were obtained. Simultaneously, the activation volumes of the <sup>95</sup>Nb solute diffusion were measured which amount to  $0.161\pm0.014\Omega$  at 1423 K and  $0.193\pm0.023\Omega$  at 1273 K. The small activation volumes indicate a strong relaxation of the vacancy. The large relaxation volume reflects the inherent weakness of the bcc lattice towards a shear in  $\langle 111 \rangle$  direction. The results provide an explanation for the absence of positron trapping in group-IV transition metals. [S0163-1829(98)02001-3]

#### I. INTRODUCTION

The study of tracer diffusion has largely passed from measurements in pure metals to investigations in intermetallic compounds, metallic glasses, amorphous solids and even polymers in the last decade. The attention which is paid to these structures is naturally justified because of their existing or expected technological importance. From a theoretical point of view the simplest solid state nevertheless is that of a monatomic crystal. The recent achievement of *ab initio* calculations of the formation volume of self-diffusion in alkali metals<sup>1,2</sup> might be regarded as to result from the simplicity of their structure. A thorough understanding of self-diffusion in pure metals is therefore a prerequisite for approaches towards more complicated structures.

The interpretation of self-diffusion in body centered cubic (bcc) metals, however, has proven difficult until today. The difficulties encountered in the interpretation, which are mainly connected with the observed convex curvature in Arrhenius presentation, are most obvious with respect to the self-diffusion behavior of  $\beta$ -Zr.

(i) Measurements of the isotope effect in  $\beta$ -Zr (Ref. 3) produced evidence against a major contribution of divacancies to self-diffusion at elevated temperatures. An analysis of the curved Arrhenius plot of self-diffusion in terms of a superposition of two diffusion mechanisms yields  $D_0^1 = 10^{-10}$  m<sup>2</sup> s<sup>-1</sup> and  $Q_1 = 0.74$  eV for the low-temperature process and  $D_0^2 = 10^{-6}$  m<sup>2</sup> s<sup>-1</sup> and  $Q_2 = 1.91$  eV for the high-temperature process.<sup>3</sup> If the first is ascribed to the monovacancy mechanism (1V) and the second to the divacancy mechanism (2V), the reproduction of the curved Arrhenius plot would require a 91% contribution of divacancies to diffusion at the melting temperature. On account of the smaller correlation factor of diffusion via divacancies in the bcc lattice ( $f_{2V}=0.34-0.49$ ,  $f_{1V}=0.727$ ) this should result in a distinct decrease of the isotope effect parameter  $E=f\Delta K$  at

elevated temperatures whereas the measurements reveal E to increase with temperature.

(ii) Another explanation of the self-diffusion behavior in bcc metals favors the monovacancy mechanism as the dominating diffusion mechanism throughout the whole experimentally accessible temperature range; it relates the Arrhenius curvature to a temperature dependence of the monovacancy parameters.<sup>4,5</sup> However, with respect to  $\beta$ -Zr this interpretation is not unambiguous either: the suggestion that the monovacancy parameters may depend on temperature in principle pertains to both the enthalpies and entropies of formation and migration. An estimation of the temperature dependence of Q indicates that  $H^m$  is stronger influenced by lattice anharmonicity than H<sup>f</sup>.<sup>6,7</sup> Thus, a temperature dependence of Q must primarily be accounted for by a temperature dependent  $H^m$ . Recent model calculations on  $H^m$ ,<sup>8</sup> based on the phonon dispersion of the pertaining metals, have revealed a slight increase of  $H^m$  from  $H^m(0.55 T_m) = 0.28$  eV to  $H^m(T_m) = 0.37$  eV for  $\beta$ -Zr. Within the same temperature interval the slope of the Arrhenius plot of Zr self-diffusion varies from  $Q(0.55T_m) = 0.77$  eV to  $Q(T_m) = 1.84$  eV, i.e., the variation of Q is about ten times stronger than the calculated change in  $H^m$ .

(iii) A recent review paper on defect parameters<sup>9</sup> has shown that the experimentally obtained monovacancy formation enthalpies of nine bcc metals scale remarkably well with their melting temperatures ( $H^f = 10^{-3}T_m \text{ eV/K}$ ). The lowtemperature slope  $Q(0.55 T_m)$  of the Arrhenius plot of  $\beta$ -Zr, however, is about three times smaller than the  $H^f$  value estimated by the above correlation. If the low-temperature diffusivity of  $\beta$ -Zr nevertheless is ascribed to the monovacancy mechanism, then it is to be asked how the obviously extraordinarily small formation enthalpy can be explained.

(iv) In contrast to group V and group VI transition metals no significant positron trapping at vacancies was observed in  $\beta$ -Zr.<sup>10,11</sup> This finding was interpreted as to result from an

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extreme smearing of the vacancy as a consequence of large lattice anharmonicity.

In view of these difficulties in understanding the Zr selfdiffusion data, we examined the pressure dependence of Zr self-diffusion. The variation of D with p provides valuable information for the interpretation of the diffusion mechanism. The activation volume  $\Delta V$  of diffusion is given by

$$\Delta V = -kT \left(\frac{\partial \ln D}{\partial p}\right)_T.$$
 (1)

An accurate experimental determination of  $\Delta V$  for  $\beta$ -Zr is difficult, because a rather small pressure effect on *D* meets with the requirements of high temperatures, precise temperature reproducibility, and clean environment. Since the radioisotope <sup>95</sup>Zr was applied in equilibrium with its radioactive daughter nuclide <sup>95</sup>Nb, the present study includes a determination of the pressure effect of Nb solute diffusion.

## **II. EXPERIMENTAL METHOD**

### A. Materials

High purity zirconium with the principal impurities O (110 wt. ppm), Fe, Nb, and Cr (50 wt. ppm each) was used for the diffusion experiments. Samples of 3 mm in height and 8 mm in diameter were cut from the cylindrical rod by spark erosion. The samples were cleaned by etching in a solution of HF, HNO<sub>3</sub>, and H<sub>2</sub>O (1:4:5 in volume). After polishing, the samples were recrystallized at 1323 K for 10 days under high vacuum conditions ( $p=0^{-6}$  Pa). The preanneal yielded a large average grain size of about 2 mm in diameter.

Radioactive zirconium was prepared by neutron activation of 90%-enriched <sup>94</sup>Zr. The obtained <sup>95</sup>Zr isotope decays into the likewise unstable isotope <sup>95</sup>Nb. The half-lives of the two isotopes are 64 and 35 days, respectively. The activated zirconium was dissolved in a few microlitres of concentrated HF and diluted in twice-distilled water. An amount of 15 kBq of the tracer solution was dropped onto the surface of each sample and was dried under an infrared lamp.

#### **B.** Diffusion anneals

The high pressure anneals were performed in a pressure cell with an internal three-zone tungsten furnace. The equipment, which is pressurized by a two stage gas pressure system, allows pressures up to 2 GPa and temperatures up to 2000 K. Purified 5N argon gas was used as pressure medium; the gas pressure was checked with a manganin gauge.

The following sample arrangement was used. The Zr samples were wrapped in Ta foil and placed in a Nb container (diameter: 10 mm, height: 41 mm) in order to protect against oxidation and Fe contamination from the steel vessel. In most of the experimental runs two specimens were annealed simultaneously to improve statistics and to check the reproducibility. The specimens were placed face to face but separated by a small Ta ring, while the remainder of the container volume was filled with Zr pellets as additional getter material. For the temperature measurement three PtRh<sub>30</sub>/PtRh<sub>6</sub> (EL 18) thermocouples were placed inside the container walls at the bottom, the middle and the top of the

container, each of them being connected to a separate controller. By use of this arrangement and a three-zone furnace the temperature gradient along the symmetry axis of the system could be appropriately balanced, and the temperature of the diffusion samples could be closely monitored. We found it useful to set the cylindrical pressure cell into a vertical position, since the influence of internal heat convection could be effectively minimized in this way.

Before pressurizing, the vessel was evacuated to  $10^{-2}$  Pa. When the pressure was raised, appropriate allowance was made for the increase in pressure on heating the cell. A standardized annealing procedure for heating up, keeping the temperature and cooling down was programmed for a set of isothermal experiments so that the total anneal time could be kept constant within one isotherm. Both temperature and pressure were recorded during the anneal for the determination of the effective anneal time. We estimate that the temperatures within one isotherm were reproduced with an uncertainty of  $\pm 0.5$  K. The pressure dependence of thermoelectric power was taken into account using the data reported by Cheng *et al.*<sup>12</sup> For this purpose, the pressure dependence of the EL 18 thermocouple was assumed to be equivalent to that of the PtRh 10Pt thermocouple.

### C. Evaluation

After the diffusion anneals, the samples were reduced in diameter with a lathe to avoid radial in-diffusion and were then sectioned with a microtome. The accurate thickness of each slice was determined from its weight, the diameter of the sample and the density (6.50 g/cm<sup>3</sup>) of the material. The decays of the isotopes <sup>95</sup>Zr and <sup>95</sup>Nb were detected by  $\gamma$  spectroscopy in a well-type intrinsic Ge detector. Corrections were made for background, Compton background, half-life and mother-daughter decays. The latter is described in detail elsewhere.<sup>13</sup> For the boundary conditions of the present experiments the solution of the diffusion equation is given by

$$c(x,t) = \frac{M}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$
(2)

with the relative specific tracer activity c, the depth coordinate x, the annealing time t, the tracer diffusion coefficient D, and the initial tracer concentration per unit area M at x=0 and t=0.

## **III. RESULTS**

Figures 1 and 2 show examples of penetration profiles of  $^{95}$ Zr self-diffusion at 1273 and 1423 K, respectively. Plotted as  $\log_{10}c$  versus  $x^2$  all profiles reveal a linear decrease of tracer activity for about three decades indicating undisturbed volume diffusion. The diffusion coefficients were obtained from a least-squares fit according to Eq. (2). They are listed in Table I. Figure 3 shows a plot of the pressure dependence of the measured diffusion coefficients. For comparison, the pressure isotherms of  $^{95}$ Zr diffusion in an equiatomic Ti-Zr (50 at. %) alloy, which were measured previously, <sup>14</sup> are also plotted.

The slope of a pressure isotherm is related to the activation volume according to Eq. (1). The corresponding least-squares fits yielded activation volumes of



FIG. 1. Penetration profiles for diffusion of  $^{95}$ Zr in  $\beta$ -Zr under pressure at 1273 K.

 $\Delta V = 0.213 \pm 0.014 \ \Omega$  at 1273 K and  $\Delta V = 0.184 \pm 0.016 \ \Omega$  at 1423 K. The atomic volume of Zr amounts to  $\Omega = 2.327 \times 10^{-29} \text{ m}^3$ . An inspection of Fig. 3 shows that the absolute pressure effect of Zr self-diffusion is less than 50%



FIG. 2. Penetration profiles for diffusion of  ${}^{95}$ Zr in  $\beta$ -Zr under pressure at 1423 K.

TABLE I. Diffusion coefficients of  $^{95}$ Zr and  $^{95}$ Nb in  $\beta$ -Zr as a function of pressure at 1273 K and 1423 K.

p	t	$D_{Zr}$	$\Delta D/D$	$D_{Nb}$	$\Delta D/D$			
10° Pa	s	m-s -	% /3 K	m-s	%			
12/3 <b>K</b>								
1.10	14880	$1.417 \times 10^{-13}$	0.71	$4.236 \times 10^{-14}$	1.64			
1.10	14880	$1.458 \times 10^{-13}$	0.34	$4.639 \times 10^{-14}$	0.68			
3.03	14880	$1.384 \times 10^{-13}$	0.78	$4.261 \times 10^{-14}$	1.76			
3.03	14880	$1.361 \times 10^{-13}$	0.39	$4.373 \times 10^{-14}$	1.19			
6.01	14880	$1.345 \times 10^{-13}$	0.61	$3.929 \times 10^{-14}$	1.97			
6.01	14880	$1.271 \times 10^{-13}$	0.37	$3.985 \times 10^{-14}$	1.28			
9.04	14880	$1.208 \times 10^{-13}$	0.61	$3.842 \times 10^{-14}$	1.32			
9.04	14880	$1.192 \times 10^{-13}$	0.29	$3.743 \times 10^{-14}$	1.64			
11.10	14880	$1.117 \times 10^{-13}$	0.43	$3.672 \times 10^{-14}$	1.74			
11.10	14880	$1.103 \times 10^{-13}$	0.22					
13.00	14880	$1.013 \times 10^{-13}$	0.54	$3.060 \times 10^{-14}$	1.60			
13.00	14880	$1.014 \times 10^{-13}$	0.39	$3.232 \times 10^{-14}$	1.85			
1423 K								
1.03	14800	$4.133 \times 10^{-13}$	0.44	$1.757 \times 10^{-13}$	1.13			
1.03	14800	$3.977 \times 10^{-13}$	0.40	$1.706 \times 10^{-13}$	0.91			
3.03	14800	$3.612 \times 10^{-13}$	0.36	$1.576 \times 10^{-13}$	0.47			
6.05	14800	$3.588 \times 10^{-13}$	0.25	$1.534 \times 10^{-13}$	0.68			
9.03	14800	$3.298 \times 10^{-13}$	0.32	$1.467 \times 10^{-13}$	1.57			
11.01	14800	$3.235 \times 10^{-13}$	0.26	$1.402 \times 10^{-13}$	0.87			
11.01	14800	$3.231 \times 10^{-13}$	0.44	$1.344 \times 10^{-13}$	1.22			
13.01	14800	$3.030 \times 10^{-13}$	0.58	$1.360 \times 10^{-13}$	0.95			
13.01	14800	$3.081 \times 10^{-13}$	0.21					

in D over the applied pressure range. It is owing to the superior reproducibility and constancy of temperature of the high pressure equipment that such a small effect could be measured reasonably.

A set of typical penetration profiles of <sup>95</sup>Nb diffusion at 1423 K is plotted in Fig. 4. Figure 5 shows the pressure isotherms of <sup>95</sup>Nb diffusion. Activation volumes of  $\Delta V = 0.193 \pm 0.023 \ \Omega$  at 1273 K and  $\Delta V = 0.161 \pm 0.014 \ \Omega$  at 1423 K were obtained.

### **IV. DISCUSSION**

The present data on the pressure dependence of Zr selfdiffusion are found to confirm the *small* activation volumes of group IV transition metals. While an activation volume of 0.33  $\Omega$  was obtained for  $\beta$ -Ti,<sup>16</sup> measurements of the pressure dependence of <sup>95</sup>Zr diffusion in an equiatomic Zr-Ti(50 at.%) alloy<sup>14</sup> yielded activation volumes between 0.31  $\Omega$  and 0.35  $\Omega$  (see also Fig. 3). The quoted self-diffusion activation volumes of group IV transition metals are well below those of the alkali metals. For the latter, activation volumes of about one half of an atomic volume have been observed.<sup>17,18</sup> Recent theoretical evidence seems to support this value: for Na, *ab initio* pseudopotential studies<sup>1</sup> yielded a monovacancy formation volume of 0.51  $\Omega$ . For Li, the calculations yielded  $\Delta V_{1V}^{f} = 0.49 \ \Omega$ ,<sup>19</sup> while a previous study<sup>20</sup> arrived at 0.52  $\Omega$ .

The question is raised how the very small activation vol-



FIG. 3. Dependence of  ${}^{95}$ Zr diffusion in  $\beta$ -Zr on pressure (open circles). The full circles represent diffusion coefficients measured at ambient pressure for the corresponding temperatures (Ref. 3). For comparison, the pressure dependence of  ${}^{95}$ Zr diffusion in Zr-Ti (50 at. %) (Ref. 14) (squares) and of Ti self-diffusion (Ref. 16) (triangles) are shown.



FIG. 4. Penetration profiles for diffusion of  $^{95}$ Nb in  $\beta$ -Zr under pressure at 1423 K.



FIG. 5. Pressure dependence of <sup>95</sup>Nb solute diffusion in  $\beta$ -Zr (open circles). The full circles represent diffusion coefficients measured at ambient pressure for the corresponding temperatures (Ref. 15).

ume of  $\beta$ -Zr can be understood. Since a measurement of the activation volume provides supplementary information about the diffusion process rather than it permits an unambiguous identification of the diffusion mechanism, the results will be discussed in conjunction with other evidence pertaining to self-diffusion in group IV transition metals.

## A. Diffusion mechanism

Irrespective of the anomalous diffusion characteristics of group IV transition metals the dominance of monovacancy diffusion throughout the high-temperature bcc phase received support from the direct determination of the elementary diffusion jump in  $\beta$ -Ti by quasielastic neutron scattering (QNS).<sup>21</sup> Measurements of the quasielastic line broadening as a function of the neutron scattering vector revealed that self-diffusion in  $\beta$ -Ti is dominated by 1/2 (111) jumps into next-neighbor vacancies. The QNS measurements were performed in the range from 1853 down to 1373 K. On the other hand, the activation volume of Ti self-diffusion<sup>16</sup> of 0.33  $\Omega$  was determined at 1273 K. Obviously both experiments suggest that even a small activation volume may reasonably be associated with the monovacancy mechanism.

As was mentioned in the Introduction, the observed increase of the isotope effect parameter E with T in  $\beta$ -Zr was interpreted as to result from an increase of the kinetic energy factor  $\Delta K$ ,<sup>3</sup> while f was assumed to be equal to the correlation factor  $f_{1V}$  of monovacancy diffusion. The small absolute values of  $\Delta K$  and its variation with temperature were reasonably explained by the low-frequent and temperature-dependent  $T_1[112]$  modes of the phonon dispersion which were shown to have particular influence on the diffusion jump.<sup>4,5,22</sup>

If one accepts from the foregoing arguments that even the small activation volume of about 0.2  $\Omega$  in  $\beta$ -Zr can be iden-

tified with diffusion via monovacancies, it remains to understand why the presumed monovacancy activation volume takes such a small value for  $\beta$ -Zr. The following sections will be devoted to this.

#### **B.** Relaxed vacancy

The formation of a vacancy in a rigid crystal would change its volume by one atomic volume  $\Omega$ . Since the real, finite crystal relaxes, the volume change accompanied by the formation of a vacancy is diminished by an amount  $\Delta V_{1V}^{rel}$ 

$$\Delta V_{1V}^{f} = \Omega - \Delta V_{1V}^{\text{rel}}.$$
(3)

Bearing in mind that the formation volume  $\Delta V_{1V}^{f}$  contributes a major part to the total activation volume,<sup>23,24</sup> the result of a very small activation volume indicates a large relaxation volume  $\Delta V_{1V}^{rel}$ .

From this point of view the present results offer a plausible explanation for the absence of positron trapping at vacancies in  $\beta$ -Zr. Extensive positron lifetime measurements in  $\beta$ -Zr<sup>10,11</sup> indicate no measurable thermal equilibrium vacancy concentration. The sensitivity of positrons to vacancies in metals arises from the absence of core electrons in a vacancy relative to the electron density of the undisturbed lattice. This results in an increased average lifetime of the positrons trapped in the bound state of the vacancy. Usually the free electrons in the region around the vacant volume will tend to flow into the vacancy, but since there is no positive charge at the vacant site this will increase the electrostatic energy. The implication is strong that a pronounced relaxation of the adjacent lattice atoms will facilitate the electron penetration of the vacancy. As a consequence, this will lead to a reduction of the attractive trapping potential.

The concept of a highly relaxed vacancy was previously postulated on the basis of phonon dispersion measurements of group IV transition metals.<sup>4,14</sup> It was argued that especially the frequency of NN atomic vibrations towards the vacancy is very low and anharmonic indicating low force constants in  $\langle 111 \rangle$  direction. The conclusion was drawn<sup>4,25</sup> that this extreme anharmonicity leads to a smearing or delocalization of the vacancy position. This conclusion has recently been reinforced by other evidence. Detailed molecular dynamics studies on the diffusion properties of  $\beta$ -Zr (Ref. 26) have indeed revealed a considerable smearing of the vacancy position. The position of a vacancy is no longer clearly defined, since at high temperatures the vacancy never comes at rest on a distinct lattice site. This is reflected in the duration of an atomic jump being larger than the time interval between two successive jumps.

#### C. Activation volume and isotope effect

Several authors<sup>27–29</sup> pointed out that the  $\Delta K$  factor entering the isotope effect parameter is likely to be correlated to the monovacancy formation volume  $\Delta V_{1V}^f$ . By definition,  $\Delta K$  denotes the fraction of translational kinetic energy associated with the passage over the saddle point that resides in the migrating atom. The  $\Delta K$  factor allows for the fact that the movement of the matrix atoms reduces the mass dependence of the jump frequency compared to the  $m^{-1/2}$  dependence predicted for a rigid lattice. According to LeClaire<sup>28</sup>

TABLE II. Comparison of the activation volume  $\Delta V$  (measured at different temperatures) with the energy factor  $\Delta K$ . The  $\Delta K$  values were evaluated from the experimentally determined isotope effect parameters *E* by assuming the correlation factor *f* to correspond to the monovacancy correlation factor  $f_{1V}$ .

Material	$\Delta V_{\mathrm{exp}}\left[\Omega\right]$	Ref.	$\Delta K$	Ref.
Cu	1.09-0.93	30	0.76-0.95	31,32
Ag	0.66 - 0.86	33	0.82-0.99	34,35
Au	0.73 - 0.77	36	0.82-0.93	37
$\alpha$ -Fe (ferromag.)	1.07 - 1.10	38	0.83	39
Na	0.41 - 0.52	18	0.52-0.36	27,18
$\beta$ -Zr	0.18 - 0.21	present work	0.40 - 0.54	3
$\beta$ -Ti-Zr	0.31-0.35	14	0.32-0.43	25

such a coupled motion of atoms will always occur, if there is any relaxation of neighboring atoms about the defect. There exists a closer correlation of  $\Delta K$  with  $\Delta V_{1V}^{f}$  than with  $\Delta V_{1V}^{m}$ , since a relaxation associated with  $\Delta V_{1V}^{f}$  always has a component parallel to the jump direction while  $\Delta V_{1V}^{m}$  is largely bound to a motion orthogonal to the jump direction. A formula derived by LeClaire<sup>28</sup> suggests

$$\Delta K \approx \left(1 + \frac{n}{3} (1 - \Delta V_{1V}^f)\right)^{-1},\tag{4}$$

where *n* is the number of atoms which are expected to be displaced by the diffusion jump. If *n* is roughly identified with the number of neighbors a migrating atom has in the saddle point configuration, insertion of  $\Delta V_{1V}^f \approx 0.2 \ \Omega$  gives  $\Delta K \approx 0.4$  for  $\beta$ -Zr. This is indeed compatible with the experimentally observed  $\Delta K$  factors at lower temperatures,<sup>3</sup> if the correlation factor for monovacancy diffusion is inserted in  $\Delta K = E/f_{1V}$ , e.g.,  $\Delta K = 0.39$  at 1189 K. Table II gives a compilation of the experimental data for those metals for which both *E* and  $\Delta V$  were measured. Except for the case of ferromagnetic iron, one finds that both  $\Delta V$  and  $\Delta K$  are much lower for the bcc than for the fcc metals.

### D. Free enthalpy of vacancy formation

When the present results are considered in conjunction with the results of isotope effect measurements in  $\beta$ -Zr (Ref. 3) and QNS experiments in  $\beta$ -Ti (Ref. 21) the balance of experimental evidence appears to favor the monovacancy mechanism throughout the bcc phase of zirconium. Nevertheless the concept of a monovacancy mechanism with temperature dependent defect quantities still suffers from two shortcomings with respect to the quantitative reproduction of the temperature dependence of Zr self-diffusion: The curvature in the Arrhenius plot seems too large to be accounted for by a temperature dependent Q only (I, item ii). Furthermore, the low temperature slope of the Arrhenius presentation demands to assume an extraordinarily low monovacancy formation enthalpy (I, item iii). The present results cannot entirely clear up these problems but at least can provide qualitative arguments for a better understanding of the above mentioned discrepancies.

The free enthalpy of vacancy formation is supposed to be lower for a crystal with large structural relaxation than if a relaxation of the atoms surrounding the vacancy is absent. It is known from theoretical calculations on atomic defects<sup>2</sup> that the relaxational contribution of the vacancy formation tends to decrease the vacancy formation enthalpy  $H_{1V}^f$ . (This can be thought of as a smoothing of the electron density at the edge of the vacant site which is expected to decrease the wavelengths of the electrons.) In addition, a large structural relaxation will lead to a further reduction of the vibrational frequencies of the atoms neighboring the vacancy and, hence, to an increase of the vibrational entropy  $S_{th}^f$  associated with the formation of the defect. This can be seen from

$$S_{\rm th}^{f} = k \, \ln \left( \frac{\Pi_{n=1}^{3N} \nu_{n}}{\Pi_{n=1}^{3N} \nu_{n}'} \right), \tag{5}$$

where the  $\nu'_n$  are the frequencies of the crystal after the introduction of the defect.

According to a suggestion of Peterson<sup>7</sup> the temperature dependence of the formation enthalpy and entropy of monovacancies may also be related to the degree of structural relaxation. A material with a small activation volume (in units of  $\Omega$ ) should reveal a more pronounced temperature dependence of the enthalpy and entropy of vacancy formation, and vice versa. Lattice anharmonicity and the accompanying thermal expansion give rise to a relaxation of the vacant site which increases with increasing temperature. The relaxation causes the vibrational frequencies  $\nu'_n$  in Eq. (5) to decrease which is coupled with a corresponding increase of  $S_{\rm th}^f$  with increasing temperature. Since  $(\partial S^f / \partial T)_p$  $=(\partial H^{f}/\partial T)_{p}/T$  it follows that  $(\partial H^{f}/\partial T) > 0$ . One expects that a large vacancy relaxation enhances the sensitivity of the vacancy formation entropy to changes in temperature. As a consequence the vacancy formation enthalpy will also be more affected to changes in temperature inasmuch as it more rapidly increases with increasing temperature than it would do in a more rigid vacancy environment. This qualitative argument may at least explain part of the observed Arrhenius curvature.

# E. Solute diffusion of <sup>95</sup>Nb in $\beta$ -Zr

Our study of the pressure dependence of Zr self-diffusion in  $\beta$ -Zr includes a simultaneous determination of Nb solute diffusion. The effect of pressure on the diffusion of <sup>95</sup>Nb was found to differ only little from the pressure dependence of self-diffusion. This finding appears to have general validity for the diffusion of substitutionally dissolved impurity atoms in group IV transition metals. Table III gives a compilation of experimental results on the pressure effect of W,<sup>40</sup> Sn,<sup>41</sup> and Zr (Ref. 42) solute diffusion in  $\beta$ -Ti and on the

TABLE III. Activation volumes of solute diffusion in bcc group- IV transition metals.

Diffusant	Matrix	T K	${\Delta V_{ m exp} \over \Omega}$	Ref.
W	<i>β-</i> Ti	1323-1673	0.28-0.41	40
Sn	β-Ti	1173-1773	0.28-0.41	41
Zr	β-Ti	1173-1773	0.22-0.36	42
Ti	$\beta$ -Ti	1273	0.33	16
Nb	$\beta$ -Zr	1273, 1473	0.19, 0.16	present work

pressure effect of Nb solute diffusion in  $\beta$ -Zr. An inspection shows that all reported activation volumes of solute diffusion in  $\beta$ -Ti fall in line with the activation volume of Ti selfdiffusion within an interval of  $\pm 30\%$ . This result is reflected in the temperature dependence of solute diffusion of Sn (Ref. 43) and Zr (Ref. 44) in  $\beta$ -Ti and of Nb diffusion in  $\beta$ -Zr:<sup>15</sup> In each case the solute diffusivity does not differ by more than a factor of five from the self-diffusivity. It is concluded that the diffusion of substitutionally dissolved atoms in group IV transition metals is obviously controlled by the matrix and is only weakly dependent on the properties (atomic radius, valence) of the solute.

### V. CONCLUSIONS

In this paper we have been concerned with the application of the radiotracer method to the determination of the dependence of self-diffusion and Nb solute diffusion in  $\beta$ -Zr pressure. on high The activation volumes are  $\Delta V = 0.213 \pm 0.014 \ \Omega$  at 1273 K and  $\Delta V = 0.184 \pm 0.016 \ \Omega$ at 1423 K for Zr self-diffusion and  $\Delta V = 0.193 \pm 0.023$   $\Omega$  at 1273 K and  $\Delta V = 0.161 \pm 0.014$   $\Omega$  at 1423 K for Nb solute diffusion. The present study helps to complete the full set of available information on the diffusion process (temperature, mass, and pressure dependence) for a second bcc metal besides the alkali metal Na. The interpretation of the activation volume is not clear cut but depends on further experimental and theoretical evidence. In combination with such other evidence the present study provides important arguments for an understanding of the low and temperature dependent defect enthalpies and entropies, the absence of positron trapping, and the isotope effect. Our results reinforce the conclusion that self-diffusion in  $\beta$ -Zr proceeds via highly relaxed monovacancies. Despite the fact that  $\beta$ -Zr is now one of those metals on which the most complete set of self-diffusion data is available, it was shown that the interpretation of the temperature dependence of self-diffusion in  $\beta$ -Zr still suffers from an appropriate quantitative description. Theoretical calculations of the monovacancy formation volume of bcc group IV transition metals appear highly desirable.

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