

Simultaneous Study of Vacancy Formation and Migration at High Temperatures in B2-Type Fe Aluminides

R. Würschum, C. Grupp, and H.-E. Schaefer

Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany

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In order to study the vacancy formation *and* migration the temperature variation and the equilibration process of the thermal vacancy concentration in B2-type Fe aluminides ($\text{Fe}_{63}\text{Al}_{37}$, $\text{Fe}_{61}\text{Al}_{39}$) were measured by means of the positron lifetime technique using a diffused ^{58}Co positron emitter. The equilibration process occurs rather slowly, indicating a low vacancy mobility. The present values for the enthalpies of vacancy formation $H_V^F = 1.04$ eV ($\text{Fe}_{63}\text{Al}_{37}$) or 0.98 eV ($\text{Fe}_{61}\text{Al}_{39}$) and migration $H_V^M = 1.7$ eV are discussed with respect to the self-diffusion mechanisms.

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Intermetallic aluminides, e.g., Fe or Ni aluminides with B2 (CsCl) structure, exhibit attractive application potentials as high-temperature structural materials [1] and, therefore, have gained rising interest recently. An assessment of the high-temperature properties, e.g., self-diffusion [2], creep, or order-disorder phenomena, requires a basic physical understanding of the properties of atomic defects as vacancies or antisite atoms in these ordered intermetallics.

For experimental studies of vacancy detection and identification, positron lifetime measurements supply a most sensitive and specific tool [3,4] and were employed for the study of thermal vacancy formation in binary intermetallic aluminides [5–8]. A comparison of the present data with the now emerging results from parameter-free *ab initio* theory [9–11] offers the prerequisites for a profound understanding of the thermal vacancy formation in these intermetallics, and, therefore, the experimental studies are of additional importance under theoretical aspects.

For a comprehensive understanding of vacancy and diffusion properties, however, both the formation *and* migration of thermal vacancies are to be considered. In the present Letter we report on a novel technique for studying the formation and migration of the same type of thermal vacancies in B2-type Fe aluminides by the observation of the equilibration process of the thermal vacancy concentration by means of positron lifetime measurements. In early efforts in this direction, fast up- and down-quenching techniques were applied in pure metals [12]. In order to prevent the drawbacks of quenching, in the present studies the equilibration process was investigated *in situ* at high temperatures. This is enabled in the unique case of B2 Fe aluminides due to the fairly *slow equilibration process* of the rather high thermal vacancy concentrations upon fast temperature changes. The vacancy data are compared to the presently available data on tracer diffusivity [2] and on atomic jump mechanisms [13].

For the thermal equilibrium positron lifetime studies (see Ref. [4]) up to 1173 K the positron emitter ^{58}Co was diffused into the FeAl specimens. For measurements

up to 1600 K a specimen with a sealed $^{22}\text{NaCl}$ source was used (see Ref. [8]). In the positron lifetime spectra with a time resolution of 260 ps (FWHM) 0.5 to 2×10^6 coincidence counts were collected. The specimen composition was determined by x-ray fluorescence and energy dispersive x-ray (EDX) techniques.

The *s*-shaped increase of the mean positron lifetime $\bar{\tau}$ with temperature in B2-type $\text{Fe}_{61}\text{Al}_{39}$ and $\text{Fe}_{63}\text{Al}_{37}$ (see Fig. 1) due to thermal vacancy formation occurs at lower temperatures than in earlier studied intermetallic aluminides. This indicates a low formation enthalpy and a high concentration of thermal vacancies. According to the simple two-state trapping model (see Ref. [4]) the positron trapping rate

$$\begin{aligned} \sigma C_V &= \frac{\bar{\tau} - \tau_f}{\tau_f(\tau_1 - \bar{\tau})} = I_1 \left(\frac{1}{\tau_0} - \frac{1}{\tau_1} \right) \\ &= \sigma \exp\left(\frac{S_V^F}{k_B T}\right) \exp\left(-\frac{H_V^F}{k_B T}\right) \end{aligned} \quad (1)$$

of thermal vacancies (concentration C_V , specific trapping rate σ) can be derived from the experimentally determined

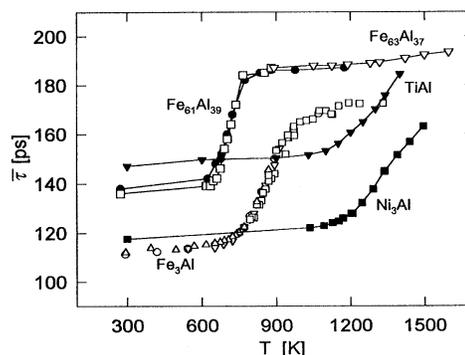


FIG. 1. Thermal vacancy formation in $\text{Fe}_{63}\text{Al}_{37}$ (\square , ∇) and $\text{Fe}_{61}\text{Al}_{39}$ (\bullet) as detected by the mean positron lifetime $\bar{\tau}$ using a diffused ^{58}Co (\square , \bullet) or a sealed $^{22}\text{NaCl}$ positron source (∇). Earlier results obtained on the transition metal aluminides Fe_3Al [5], TiAl [8], and Ni_3Al [6] are shown for comparison.

values of $\bar{\tau}$ and the positron lifetimes in the free ($\tau_f = [(1 - I_1)\tau_0^{-1} + I_1\tau_1^{-1}]^{-1}$) and vacancy trapped (τ_1 , intensity I_1) states where S_V^F and H_V^F denote the effective entropy and enthalpy of vacancy formation, respectively.

The free positron lifetime $\tau_f(300 \text{ K}) = 121 \text{ ps}$ determined for $\text{Fe}_{61}\text{Al}_{39}$ from the analysis of the lifetime spectra appears to be slightly higher than in pure α -Fe (106 ps [5]) or Fe_3Al (112 ps [5]). The positron lifetime $\tau_1 = 187 \text{ ps}$ in thermal vacancies measured here is similar to the single positron lifetime component $\tau_1 = 180 \text{ ps}$ observed after electron irradiation of $\text{Fe}_{61}\text{Al}_{39}$ (electron energy $E_e = 2.5 \text{ MeV}$, electron dose $\Phi = 9 \times 10^{22} \text{ m}^{-2}$) and coincides with the values calculated for Fe_3Al recently [14].

From the data for $\text{Fe}_{61}\text{Al}_{39}$ or $\text{Fe}_{63}\text{Al}_{37}$ in Fig. 1 between 660 and 740 K the apparent enthalpies of vacancy formation

$$H_V^F = 0.98 \pm 0.07 \text{ eV} \quad \text{or} \quad 1.04 \pm 0.07 \text{ eV} \quad (2)$$

with the preexponential factors

$$\sigma \exp\left(\frac{S_V^F}{k_B}\right) = 1.2 \times 10^{17} \text{ s}^{-1} \quad \text{or} \quad 2.7 \times 10^{17} \text{ s}^{-1} \quad (3)$$

can be derived, yielding, similarly as in Fe_3Al [5], high apparent entropies of vacancy formation

$$S_V^F = 5.7k_B \quad \text{or} \quad 6.5k_B, \quad (4)$$

respectively, if a temperature invariant $\sigma = 4 \times 10^{14} \text{ s}^{-1}$ as in pure metals [4] is assumed.

The vacancy formation enthalpies of Eq. (2) are in good agreement with the values derived earlier from resistivity studies after quenching [15] and appear to be typical for $B2$ aluminides [16]. These values are considerably lower than in the closer-packed intermetallic compounds TiAl [8] and Ni_3Al [6,7] (Table I), which may be understood by the lower coordination number and the lower number of bonds per atom in the $B2$ structure. According to theoretical studies vacancies in $B2$ -type Fe aluminides are predominantly formed on the Fe sublattice, together with an even higher concentration of antisite atoms on either sublattice [9,10,16,19,20].

TABLE I. Effective vacancy formation enthalpies H_V^F and vacancy migration enthalpies H_V^M in transition metal aluminides as determined by positron annihilation (see Fig. 1).

Structure	H_V^F (eV)	H_V^M (eV)	
$\text{Fe}_{61}\text{Al}_{39}$	$B2$	0.98 ± 0.07	1.7 ± 0.2
$\text{Fe}_{63}\text{Al}_{37}$	$B2$	1.04 ± 0.07	1.7 ± 0.2
Fe_3Al	$D0_3$	1.18 ± 0.04^a	1.3 ± 0.1^c
TiAl	$L1_0$	1.41 ± 0.06^b	
Ni_3Al	$L1_2$	1.80 ± 0.06^c	
Fe_3Si	$D0_3$	0.80 ± 0.1^d	

^aReference [5].

^bReference [8].

^cReference [7].

^dReference [17].

^eAfter quenching, Ref. [18].

The thermal vacancy concentration obtained by an extrapolation of the present data to 1173 K ($C_V = 1.8 \times 10^{-2}$) is, with regard to the experimental uncertainties, similar to that from differential thermal expansion studies at this temperature (6×10^{-3} [21]) which justifies the above assumption for σ . A decrease of the vacancy formation enthalpy at high temperatures as invoked from differential dilatometry [21,22] may be associated with increasing disorder or a more complex process at higher temperatures.

The obviously high concentrations of thermal vacancies raise the question about the formation of divacancies at high temperatures. The 6 ps increase of $\bar{\tau}$ at the $B2$ - $A2$ (1473 K) phase transition indicates a doubling of the free volume size of the positron trap [23]. This may be considered as evidence for divacancy formation, since in the disordered $A2$ phase vacancy pairs can be formed on nearest-neighbor sites and, therefore, provide a larger free volume for a positron compared to divacancies in the $B2$ phase occupying next-nearest-neighbor sites on the Fe sublattice predominantly. With the assumption of a *high* divacancy binding energy $H_{2V}^B \approx 0.5 \text{ eV}$, as predicted theoretically [9], and a divacancy binding entropy $S_{2V}^B = 1k_B$, slightly reduced values for the vacancy formation enthalpy ($H_V^F \approx 0.89 \text{ eV}$) and entropy ($S_V^F = 4.2k_B$) would be estimated from the positron lifetime data on $\text{Fe}_{61}\text{Al}_{39}$ in comparison to the analysis presented above according to Eq. (1).

It should be emphasized that in the present FeAl alloys even below the onset temperature $T_t = 620 \text{ K}$ of the increase of $\bar{\tau}$ (Fig. 1) partial positron trapping at vacancies ($\bar{\tau} > \tau_f = 121 \text{ ps}$) is observed in the positron lifetime spectra even after long-term annealing at 623 K. This demonstrates the presence of residual vacancies due to a pretty low vacancy diffusivity. Indications for this were found earlier from the variation of the plastic behavior of Fe aluminides with thermal pretreatment [24–26]. The low vacancy diffusivity at the very concentrations where thermal vacancies can be detected by positrons provides here the opportunity to study vacancy migration on a time scale of hours by means of the equilibration process of the thermal vacancy concentration after fast temperature changes (632–723 K).

In Fig. 2 the time dependence of the mean positron lifetime after fast cooling from an initial temperature $T_i = 770 \text{ K}$ to various final temperatures T_f is shown where the trapping rates σC_V are given by Eq. (1). In the case of a monomolecular diffusion-limited reaction for the disappearance of vacancies at homogeneously distributed sinks [12], the equilibration of the vacancy concentration obeys the relationship

$$\Delta C_V(t) = C_V(t) - C_f = (C_i - C_f) \exp\left(-\frac{t}{t_E}\right), \quad (5)$$

where C_i and C_f denote the initial and final equilibrium vacancy concentrations, respectively. In a simple case the

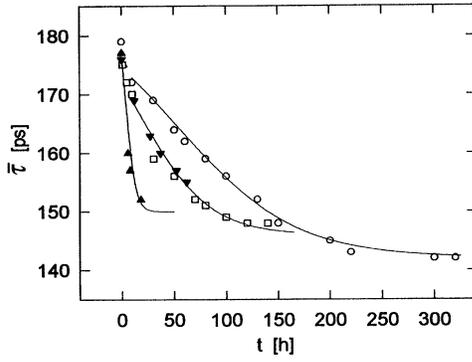


FIG. 2. Mean positron lifetime $\bar{\tau}$ measured on $\text{Fe}_{61}\text{Al}_{39}$ during equilibration after rapid cooling from the temperature $T_i = 770$ K to the final temperature $T_f = 673$ K (Δ), 654 K (\square), 638 K (∇), or 623 K (\circ). Measuring time per positron lifetime spectrum was 3–10 h. The fitted lines were calculated with the time constants t_E for equilibration as determined from Eq. (5) (see Fig. 3).

rate constant t_E^{-1} can be written as

$$t_E^{-1} = \xi \nu_0 \frac{Z}{N} \exp\left(\frac{S_V^M}{k_B}\right) \exp\left(-\frac{H_V^M}{k_B T}\right), \quad (6)$$

where the quantities S_V^M , H_V^M , Z , N , ξ , and ν_0 denote the vacancy migration entropy or enthalpy, the coordination number, the mean number of jumps per vacancy to a sink, a geometrical factor, and an attempted frequency of the order of the Debye frequency, respectively. A fit of Eqs. (5) and (6) to the slopes of $\Delta(\sigma C_V(t))$ (Fig. 3) yields for the alloy $\text{Fe}_{61}\text{Al}_{39}$ the vacancy migration enthalpy

$$H_V^M = 1.7 \pm 0.2 \text{ eV} \quad (7)$$

along with a preexponential factor

$$\xi \nu_0 \frac{Z}{N} \exp\left(\frac{S_V^M}{k_B}\right) = 1.9 \times 10^8 \text{ s}^{-1}. \quad (8)$$

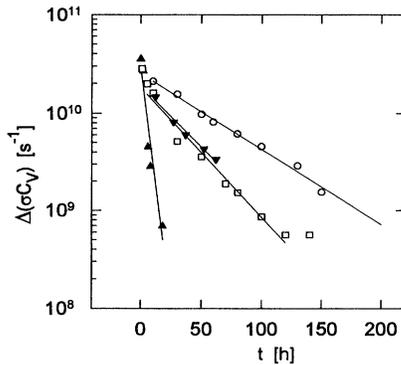


FIG. 3. Change $\Delta(\sigma C_V(t))$ [Eq. (5)] of the positron trapping rate $\sigma C_V(t)$ after rapid cooling from the temperature $T_i = 770$ K to the final temperature $T_f = 673$ K (Δ), 654 K (\square), 638 K (∇), or 623 K (\circ) and the positron trapping σC_f at the respective final temperature after equilibration as determined from $\bar{\tau}$ [Fig. 2, Eq. (1)] with $\tau_1 = 187$ ps and $\tau_f(T) = 121 \times [1 + 10^{-4} \text{ K}^{-1} \times (T - 293 \text{ K})]$ ps (see text).

Similar values are obtained for $\text{Fe}_{63}\text{Al}_{37}$. Assuming $\nu_0 = 10^{13} \text{ s}^{-1}$, $Z = 8$, $S_V^M = 1k_B$, and $\xi = 1$, a mean number $N \approx 10^6$ of jumps per vacancy to sinks is estimated [Eq. (8)].

It should be pointed out that the effective values of H_V^M and H_V^F both pertain to the same type of vacancy, which is identified by the positron lifetime τ_1 . In contrast to pure metals with a ratio $H_V^F/H_V^M > 1$, in the present case the two quantities can be measured at the same temperature in or near thermal equilibrium conditions. This is due to the slow diffusivity of the thermally formed vacancies, which originates from both the low temperatures for vacancy detection (low H_V^F) and the relatively high H_V^M value.

The high value of H_V^M , which is identical to the activation energy derived from resistivity studies for defect annealing after quenching in $\text{Fe}_{60}\text{Al}_{40}$ [27–29], may reflect a more complex atomic jump mechanism in intermetallic compounds compared to pure metals. For the atomic self-diffusion in *B2*-type intermetallic compounds various vacancy mechanisms including complex six-jump cycles have been proposed (for reviews see [30]). Most recently, evidence has been derived from quasielastic Mössbauer spectroscopy that the diffusion of Fe atoms occurs via the Al sublattice by means of next-nearest-neighbor jumps with the residence time of the Fe atoms in the antisite configuration being correlated with the ordering energy, i.e., with the deviation from stoichiometry [13]. In this case, the low vacancy mobility may be considered as a consequence of the vacancy migration process via next-nearest-neighbor sites involving vacancies on the Al sublattice with a low equilibrium concentration according to theoretical results [9,10,16,19,20]. With increasing Fe content structural antisite atoms on the Al sublattice serve as bridges over which vacancies can migrate without changing the degree of order [31].

For the Fe self-diffusivity in $\text{Fe}_{59.5}\text{Al}_{40.5}$ between 1200 and 1427 K, the relationship

$$D^{\text{Fe}} = 0.083 \times \exp\left(-\frac{3.0 \text{ eV}}{k_B T}\right) \text{ m}^2 \text{ s}^{-1} \quad (9)$$

was reported [2]. An extrapolation to the onset temperature $T_i = 770$ K of positron saturation trapping at thermally formed vacancies yields a diffusion coefficient $D^{\text{Fe}} = 1.9 \times 10^{-21} \text{ m}^2 \text{ s}^{-1}$. If we apply, on the other hand, the simple relationship

$$D^{\text{SD}} = d^2 \nu_0 \exp\left(\frac{S_V^F + S_V^M}{k_B}\right) \exp\left(-\frac{H_V^F + H_V^M}{k_B T}\right), \quad (10)$$

assuming a correlation factor of $f = 1$ for self-diffusivity mediated by thermal vacancies, we may derive from the present data [Eqs. (2), (4), and (7)] a value $D^{\text{SD}}(770 \text{ K}) = 1.3 \times 10^{-21} \text{ m}^2 \text{ s}^{-1}$. Here, a vacancy migration entropy $S_V^M = 1k_B$ and a preexponential jump factor $\nu_0 = 10^{13} \text{ s}^{-1}$ of the order of the Debye frequency were assumed with a nearest-neighbor distance $d = 0.24 \text{ nm}$ [Eq. (10)]. The results from positron

lifetime and tracer diffusion studies, therefore, appear to be compatible with a vacancy-mediated diffusion mechanism. With the available techniques for measuring low self-diffusivities [32] extended to the same low-temperature range, where the formation and migration of vacancies are studied by positron lifetime measurements, a more detailed assessment of this issue might emerge.

In conclusion, we may emphasize that positron lifetime measurements of the equilibration of the thermal vacancy concentration enable in a unique way a simultaneous study of both vacancy formation and migration at the same temperature. These studies may be extended to higher temperatures by measuring shorter equilibration time constants by means of pulse-heating techniques [33]. In addition, measurements after temperature up-pulsing or down-pulsing could supply information on vacancy sources or sinks, respectively [34].

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