PHYSICAL REVIEW B VOLUME 54, NUMBER 2 1 JULY 1996-II

Characterization of radiation-induced lattice vacancies in intermetallic compounds by means of positron-lifetime studies

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(Received 28 December 1995; revised manuscript received 19 March 1996)

In the present paper a characterization of atomic vacancies in intermetallic compounds is given by means of positron-lifetime measurements after electron irradiation and comparison with the states after preparation, after long-time annealing, or in high-temperature equilibrium. In TiAl, Ti_3Al, and Ni_3Al no structural vacancies (detection limit $C_V = 10^{-6}$) are observed at ambient temperature. This confirms that in these compounds slight deviations from stoichiometry are compensated by antisite atoms. In the Al-poor $B2$ alloys FeAl and NiAl, on the other hand, remnant vacancies exist due to the high thermal equilibrium vacancy concentrations and their slow diffusivities. The kinetics of vacancy elimination in FeAl and NiAl is discussed. A substantial temperature dependence of the positron lifetime in vacancies is detected in close-packed intermetallics which is attributed to an increased atomic relaxation or partial positron detrapping at high temperatures. In contrast to that, the temperature dependence of the positron lifetime in vacancies is small in the open-structured $B2$ aluminides. The lifetimes τ_f of free delocalized positrons in transition-metal aluminides and in NiZr and NiTi can be correlated to those of the pure components, taking into account the densities of valence electrons. For the positron lifetimes τ_1 of vacancies in intermetallic compounds, values of $\tau_1/\tau_f = 1.5–1.7$ are observed similar as in the pure metals. Annealing studies of $B2$-FeAl after electron irradiation yield time constants for the disappearance of vacancies identical to those deduced recently for the equilibration of thermal vacancies. In electron-irradiated Ti aluminides annealing processes at 250 K and 450 K are observed where the latter process is tentatively attributed to long-range migration of vacancies. [S0163-1829(96)00426-2]

I. INTRODUCTION

Alloy systems with intermetallic compounds are the subject of comprehensive investigations under aspects such as the attractive high-temperature mechanical properties of transition-metal aluminides or the formation of novel and metastable microstructures as in the case of quasicrystalline or amorphous alloys. For both aspects lattice vacancies or vacancy-type free volumes play an important role. On the one hand, the thermal formation and migration of lattice vacancies determine the material transport properties at high temperatures, e.g., self-diffusion, or creep. On the other hand, vacancy-type defects may represent structural elements in intermetallic compounds or disordered alloys.

To both types of questions positron-lifetime spectroscopy was applied recently as a sensitive tool[1] to the study of thermal vacancy formation in transition-metal aluminides [Fe_3Al (Ref. 2), FeAl (Ref. 3), TiAl (Ref. 4), Ti_3Al (Ref. 5), and Ni_3Al (Refs. 6–8)] and in order to characterize structural free volumes in crystalline or quasicrystalline Al-rich[9,10] or amorphous Ni-based alloys.[11]

For a more detailed and comprehensive characterization of vacancy-type defects in these materials, the present paper aims at a positron-lifetime study of vacancies in transition-metal aluminides and in the intermetallic compounds NiZr and NiTi after electron irradiation (Sec. III A). As demonstrated earlier in the cases of GaAs (Ref. 12) or SiC (Ref. 13), positron-lifetime measurements in binary-crystalline compounds after low-temperature electron irradiation near or well above the threshold of atomic displacement may provide specific information on vacancy-type defects on the two sublattices. Hence, they may contribute to the assessment of thermal defects at high temperatures or of structural vacancies (Sec. III A 2).

The determination of the characteristic positron lifetimes τ_f or τ_1 in the free or the vacancy-trapped states of intermetallic compounds and the constituent pure metals yields, furthermore, insight into the systematics of positron annihilation parameters (Sec. III A 3). This is of particular interest for an assessment of theoretical data and is helpful for the characterization of vacancy-type defects in disordered materials.

A further objective of the present work comprises the study of the annealing behavior of radiation-induced vacancies in Fe- and Ti-aluminides (Sec. III B). From this type of measurement additional information on defect migration and the mechanisms of self-diffusion can be derived by means of a comparison with high-temperature vacancy formation and self-diffusion studies.

The details of the technique of positron-lifetime spectroscopy are described elsewhere.[14] In the simplest case of the applicability of a two-state trapping model,[15] the mean positron lifetime

$$\overline{\tau} = \tau_f \times \frac{1 + \sigma C_V \tau_1}{1 + \sigma C_V \tau_f} \tag{1}$$

is given by the characteristic time constants τ_f, τ_1, the atomic concentration C_V of vacancies, and the specific positron trapping rate σ.

II. EXPERIMENTAL PROCEDURE

Specimen platelets ($7\times 9\ \mathrm{mm}^2$) were cut from pure metals (Zr 99.8 at. %, Ti 99.99 at. %, Goodfellow) or from the same intermetallic materials which were used for the high-temperature studies of thermal vacancies in $B2$-$\mathrm{Fe}_{61}\mathrm{Al}_{39}$ (Ref. 3), γTiAl (Ref. 4), $\alpha_2\mathrm{Ti}_3\mathrm{Al}$ (Ref. 5), and Ni-aluminides (Ref. 8) or for the structural studies of amorphous alloys [NiZr, NiTi (Ref. 11)].

Low-temperature electron irradiation ($E_{e^-}=0.4,0.55$ MeV, T_{irrad} = 120–140 K; $E_{e^-}=2.5$–2.9 MeV, T_{irrad} = 85–95 K) was performed at the Stuttgart Dynamitron accelerator. The positron-lifetime spectra (2×10^6 coincidence counts) were measured with a sandwiched ^{22}NaCl positron source by means of a fast-slow $\gamma\gamma$ spectrometer [time resolution full width at half maximum (FWHM) 240 ps] and numerically analyzed (see Refs. 12,16). Annealing experiments above ambient temperature were performed under high vacuum ($p\leqslant 10^{-4}$ Pa) after removing the positron source from the specimen platelets. For long-time annealing ($t_a>24$ h) the specimens were sealed off in glass ampoules.

III. RESULTS AND DISCUSSION

A. Characterization of lattice vacancies

1. Free positron lifetimes and detection of vacancies in the as-prepared specimens

In close-packed $L1_0$-type $\mathrm{Ti}_{48.5}\mathrm{Al}_{51.5}$, $D0_{19}$-type $\mathrm{Ti}_{66.4}\mathrm{Al}_{33.6}$, and $L1_2$-type $\mathrm{Ni}_3\mathrm{Al}$, positron lifetimes rather similar to that in the pure transition metals (Ti, Ni) occur after preparation. These lifetimes characterize the ''free'' delocalized state of positrons in the crystal lattices (Table I, Fig. 1, see Sec. III A 3) and demonstrate the absence of quenched-in thermal or structural vacancies (detection limit of atomic concentration 10^{-6}; see below). This supports theoretical predictions for these compounds according to which deviations from the stochiometric compositions on both sides give rise to antisite atoms rather than to structural vacancies.[5,8,30]

In the open-structured $B2$-type Fe- or Ni-aluminides, on the other hand, vacancies are detected after preparation of the specimens. This is demonstrated by the single-component positron-lifetime spectra with time constants $\tau_1=187$–200 ps (Fe-Al, Fig. 2) or $\tau_1=166$–180 ps (Ni-Al, Fig. 3). These lifetimes are similar to the theoretical values for vacancies, e.g., in Fe-Al (see Table I) and much higher than the free positron lifetimes expected from a comparison with the free lifetimes in pure Fe or Ni (see Table I and Sec. III A 3). They are, therefore, ascribed to saturation trapping and annihilation of positrons at vacancies.

In the Fe-rich Fe aluminides ($C_{\mathrm{Al}}\leqslant 39$ at. %) these vacancies can be mainly eliminated by means of long-time annealing at $T_a=633$ K (340 h). This is indicated by the decrease of the mean positron lifetime $\overline{\tau}$ which arises from a short-time constant due to partial positron annihilation in the free state with a lifetime $\tau_f=121$ ps (see Fig. 2). We conclude, therefore, that the vacancies in the as-prepared state of the Fe aluminides are introduced by quenching due to the low diffusivity of thermal vacancies[3] during cooling rather than by deviations from stochiometry. This is in agreement with theoretical results which predict antisite atoms ($\mathrm{Fe}_{\mathrm{Al}}$, $\mathrm{Ni}_{\mathrm{Al}}$) as structural defects on the transition-metal-rich side of the $B2$ aluminides.[8,31] The removal of vacancies at higher annealing temperatures is restricted by the early onset of thermal vacancy formation[3] (Fig. 2, compare $T_a=633$ K and 733 K). Moreover, the removal of vacancies becomes less efficient with increasing Al content as indicated by the increase of $\overline{\tau}$ (Fig. 2). This is due to a decrease of the vacancy formation enthalpy[3,8,32] or an increase of the vacancy migration enthalpy[33,34] with increasing Al content.

In $B2$-NiAl, in contrast to Fe-Al, the high positron lifetimes are persistent even after long-time annealing (see Table I, Fig. 3). This demonstrates that in $B2$-NiAl on both sides of the stoichiometric composition vacancy concentrations $C_V\geqslant 10^{-4}$ above the limit of saturation trapping of positrons occur. On the Ni-poor side, the saturation trapping of positrons originates from structural vacancies in high concentrations.[8,31] In Ni-rich NiAl, however, antisite atoms rather than structural vacancies are expected like in Fe-Al (see above). The high positron lifetimes (Fig. 3) in that case are ascribed to saturation positron trapping at quenched-in thermal vacancies. These vacancies can hardly be removed as shown in the following for $\mathrm{Ni}_{53}\mathrm{Al}_{47}$.

(a) Saturation positron trapping, i.e., positron annihilation exclusively from vacancies, is typically observed above a positron trapping rate of $\sigma C_V=3\times 10^{10}\ \mathrm{s}^{-1}$ (see, e.g., Ref. 20). Together with a specific trapping rate $\sigma=4\times 10^{14}\ \mathrm{s}^{-1}$ as in pure metals[1] this yields a lower limit for the available vacancy concentration of $C_V\geqslant 7.5\times 10^{-5}$.

(b) Concentrations of thermal vacancies above this limit exist in $\mathrm{Ni}_{53}\mathrm{Al}_{47}$ at high temperatures (e.g., $C_V=2\times 10^{-4}$ at 770 K) due to the low activation enthalpy $H_V^F=0.67$ eV for vacancy formation.[35]

(c) These vacancies are easily quenched in and hardly removed due to a high migration enthalpy $H_V^M=Q^{\mathrm{SD}}-H_V^F=2.1$ eV for Ni vacancies as derived from H_V^F [item (b)] and the activation enthalpy $Q^{\mathrm{SD}}=2.77$ eV for Ni self-diffusion.[36] The disappearance of vacancies may be characterized by the time constant

$$t_E=t_0\exp(H_V^M/k_BT_A). \tag{2}$$

Making use of the preexponential factor $t_0=5\times 10^{-9}$ s determined for $B2$-$\mathrm{Fe}_{61}\mathrm{Al}_{39}$ (Ref. 3) the time constant $t_E=79$ h can be determined for annealing out of vacancies at 770 K in $\mathrm{Ni}_{53}\mathrm{Al}_{47}$. This means that at 770 K the equilibration [$C_V=2\times 10^{-4}$, item (b)] can be attained within the experimental annealing time of 120 h (see Fig. 3). The residual vacancy concentration above the limit of positron saturation trapping [item (a)] is, however, retained at lower temperatures because the annealing is too slow.

A further important aspect of the positron-lifetime measurements in the as-prepared state pertains to the variation of the positron lifetime τ_1 in vacancies with the composition of $B2$-NiAl (Fig. 3) or $B2$-FeAl (Fig. 2). From this variation information on vacancy agglomeration or complexes of vacancies with neighboring Ni or Fe antisite atoms may be deduced. An increasing contribution of vacancy agglomerates with an elevated positron lifetime (e.g., divacancies) on the Al-rich sides is expected from an agglomeration of structural vacancies of increasing concentration. On the other hand, complexes of Ni (or Fe) vacancies with Ni (or Fe)

TABLE I. Positron lifetime in the free state (τ_f) and in the vacancy-trapped state ($\tau_{1,\mathrm{irrad}}$) after electron irradiation (energy $E_{e^-}=2.0$–2.9 MeV) and annealing (temperature T_a) or in high-temperature thermal equilibrium ($\tau_{1,\mathrm{therm}}$) as well as theoretical values for the positron lifetime in monovacancies ($\tau_{V,\ \mathrm{theo}}$) of intermetallic compounds and the constituent pure metals. ρ_{el} denotes the valence electron density and N_e the mean number of the outer s, p, and d electrons per atom. Experimental uncertainty $\Delta\tau=\pm 2$ ps.

	Structure	τ_f [ps]	$\tau_{1,\mathrm{irrad}}$ [ps] (T_a [K])	$\tau_{1,\mathrm{therm}}$ [ps]	$\tau_{V,\ \mathrm{theo}}$ [ps]	ρ_{el} [nm^{-3}]	N_e
$Ti_{51.5}Al_{48.5}$	$L1_0$	146	220 (90/300)	211 [a]		216	3.5
$Ti_{66.4}Al_{33.6}$	$D0_{19}$	147	223 (140/300)	223 [b]		221	3.7
$Ti_{77.1}Al_{22.9}$	$D0_{19}$	147				223	3.8
Ni_3Al	$L1_2$	109	181 (90) 182 [e]	157 [c]	V_{Ni}: 177 [d] V_{Al}: 175 [d]	732	8.25
$Fe_{76.3}Al_{23.7}$	$D0_3$/ $B2/A2$	112 [f]		171 [f]	V_{Fe}:186 [g] V_{Al}:184 [g]	566	6.75
$Fe_{75}Si_{25}$	$D0_3$	109 [h]		175 [h]		624	7
$Fe_{61}Al_{39}$	$B2$	121 [i]	180 (90/300)	187 [j]		491	6.0
$Ni_{49.5}Al_{50.5}$	$B2$		184 [k] (90/300)			542	6.5
$Ni_{52}Al_{48}$			172 [k] (90/300)				
$Ni_{60}Al_{40}$			167 [k] (90/300)				
NiTi	$B2$	132 [l]	197 (300)			384	7
NiZr	$B33$	142 [m]	197 (300)			432	7
Ti	hcp	146	220 (90)		146 [n]	227	4
Zr	hcp	159	219 (300)		159 [n]	172	4
Fe	bcc	106 [o]	175 [p]	144 [q]	190 [r]	680	8
Ni	fcc	101 [s]	160 (90)	152 [s]	184 [r]	834	10
Al	fcc	163 [t]	251 [t]	248 [t]	253 [r]	181	3

[a] Brossmann *et al.* (Ref. 4).
[b] Value taking into account frequent positron detrapping and retrapping, Würschum *et al.* (Ref. 5).
[c] Badura-Gergen (Ref. 8).
[d] Puska (Ref. 17).
[e] Wang *et al.* (Ref. 18).
[f] Schaefer *et al.* (Ref. 2).
[g] Jirásková *et al.* (Ref. 19).
[h] Kümmerle *et al.* (Ref. 20).
[i] Derived from two-component spectra analysis (Fig. 2).
[j] Würschum *et al.* (Ref. 3).
[k] Saturation value before and after irradiation (Fig. 3).
[l] Würschum *et al.* (Ref. 21).
[m] Würschum *et al.* (Ref. 22).
[n] Puska (Ref. 23).
[o] Schaefer and Würschum (Ref. 24).
[p] Vehanen *et al.* (Ref. 25).
[q] Shirai *et al.* (Ref. 26).
[r] Puska and Nieminen (Ref. 27).
[s] Franz *et al.* (Ref. 28).
[t] Schaefer *et al.* (Ref. 29).

antisite atoms are anticipated on the Al-poor side due to a high concentration of structural Ni (or Fe) antisite atoms and the predominant formation of thermal vacancies on the transition-metal sublattice (see Ref. 3 and references therein). Therefore, the lowering of the positron lifetime to the value for vacancies in pure Ni (or Fe; see Table I) may arise from the additional contribution of electrons to the positron annihilation rate due to the additional transition metal atoms in the direct neighborhood.

The behavior of the positron lifetime τ_1 in residual vacancies during annealing in $B2$-FeAl differs from that in NiAl. In FeAl the vacancy migration enthalpy $H_V^M=1.7$ eV is also high[3] but lower than the above estimates for NiAl. This explains the increase of τ_1 upon annealing (see Fig. 2) in terms of the formation of small vacancy clusters. Moreover, *ab initio* calculations of the vacancy binding energy suggest a stronger tendency for vacancy agglomeration in the case of FeAl in comparison to NiAl.[37]

2. Positron lifetimes in radiation-induced vacancies compared to high-temperature thermal vacancies

From a comparison of vacancies induced by low-temperature electron irradiation or formed at high temperatures information on the variation of the positron lifetime in

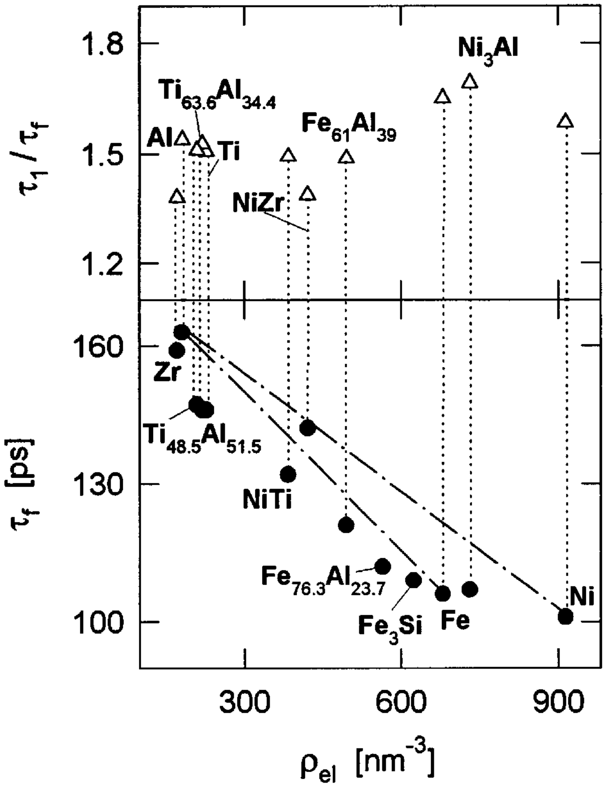

FIG. 1. Ratio of the positron lifetimes in the vacancy-trapped state ($\tau_{1,\mathrm{irrad}}$) after electron irradiation and in the free state (τ_f) as well as τ_f in intermetallic compounds and the constituent pure metals. The valence electron density $\rho_{el}=\rho_{at}N_{el}$ is given by the atomic density ρ_{at} and the mean number N_{el} of outer s, p, and d electrons per atom (see Table I).

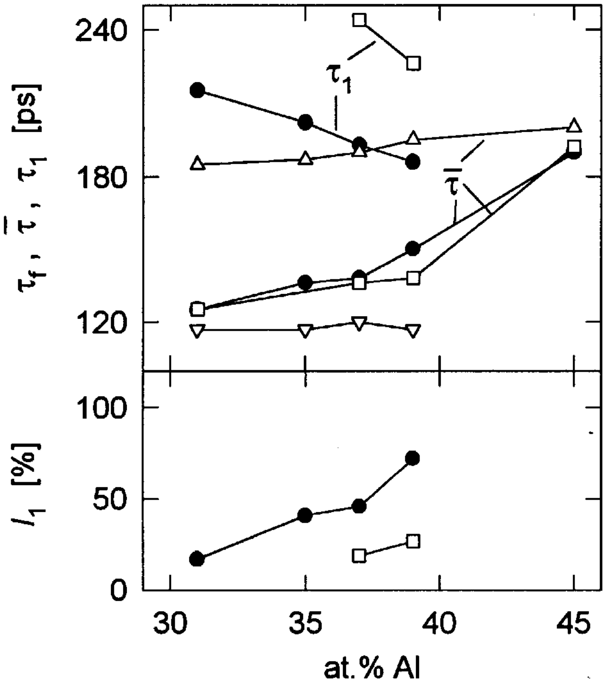

FIG. 2. Mean positron lifetime $\overline{\tau}$ and positron-lifetime component τ_1 with relative intensity I_1 due to trapping at vacancies measured at ambient temperature in the as-prepared state [(Δ) $\overline{\tau}=\tau_1$] and after long-time annealing [(●) 723 K, 100 h, (□) 623 K, 340 h] of unirradiated Fe-aluminides. The free positron lifetime ($\tau_f=[(1-I_1)\tau_0^{-1}+I_1\tau_1^{-1}]^{-1}$) (∇) according to the two-state trapping model was derived from the time constants τ_0 and τ_1 and the relative intensity I_1 after annealing.

vacancies with temperature or with the sublattice of the binary compound may be deduced.

Thermal vacancies in intermetallic aluminides are predominantly formed on the transition metal sublattice (see Refs. 3,5,8 and references therein). After irradiation, however, Al vacancies are expected to be selectively generated if the electron energy is sufficiently low. This is concluded from the displacement threshold energies lower for Al atoms than for Ni atoms.[38] Higher electron energies will induce vacancies on both sublattices.

In Ni_3Al or $Ti_{48.5}Al_{51.5}$ practically the same positron lifetimes $\tau_{1,\mathrm{irrad}}$ for the vacancy-trapped state were found after irradiation with high-energy ($E_{e^-}\sim 2.5$ MeV) and low-energy electrons (Ni_3Al, $E_{e^-}=0.44$–0.55 MeV; $Ti_{48.5}Al_{51.5}$, $E_{e^-}=0.44$ MeV). This conjectures that the positron lifetimes in vacancies on either sublattice are similar which is in agreement with recent theoretical studies (see Table I) in Ni_3Al (Ref. 17) and Fe_3Al (Ref. 19).

In Ni_3Al and to some extent in $Ti_{51.5}Al_{48.5}$ the positron lifetimes in radiation-induced vacancies at low temperature are higher than in high-temperature thermal vacancies (see Table I). This behavior is as also observed in pure Fe or Ni (Table I). Since the difference of the positron lifetimes in vacancies on the two sublattices appears to be negligible (see above), this change is attributed to an increased relaxation of vacancies at high temperatures or a partial positron detrapping from high-temperature thermal vacancies. Strong evidence for fast positron detrapping and retrapping at thermal vacancies could be derived from recent high-temperature studies of $D0_{19}$-$Ti_{66.4}Al_{33.6}$ which is close packed, too.[5]

Compared to the close-packed intermetallic alloys where vacancies appear to be prone to a decrease of the positron lifetime and a loosening of the positron binding a different situation prevails in open-structured $B2$-FeAl. In this compound no temperature variation of the positron lifetime τ_1 in vacancies occurs; i.e., similar τ_1 values are observed after electron irradiation ($E_{e^-}=2.5, 2.6$ MeV; Fig. 4), after quenching, or in high-temperature thermal equilibrium (see Table I). In addition, this result indicates similar positron lifetimes in vacancies on either sublattice.

The same behavior can be deduced in the case of $B2$-NiAl from the following observations.

(i) In $Ni_{50}Al_{50}$, the value $\tau_1 = 184$ ps at ambient temperature due to remnant quenched-in vacancies remains nearly unchanged up to 1300 K (Ref. 8) where abundant thermal vacancy formation occurs.[35]

(ii) The same positron lifetime is observed in quenched-in or radiation-induced vacancies in NiAl.

The latter item follows from the observation that the positron lifetime in NiAl with a quenched-in vacancy concentration of $C_V=2.0\times10^{-4}$ (see Sec. III A 1) is unchanged upon irradiation ($E_{e^-}=2.6$ MeV, electron dose $\phi=10^{23}$ m^{-2}). The irradiation of $Fe_{61}Al_{39}$ with a considerably lower dose ($\Phi=5.6\times10^{22}$ m^{-2}) gives rise to saturation trapping of positrons, i.e., to a concentration $C_V>7.5\times10^{-5}$ of radiation-induced vacancies (see Fig. 4 and Sec. III A 1). Therefore, the radiation-induced vacancies in NiAl should be visible in

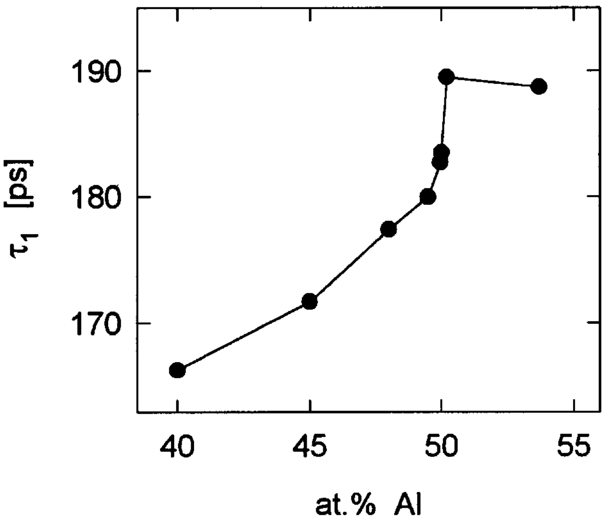

FIG. 3. Single positron-lifetime component τ_1 in well-annealed Ni-aluminides before and after electron irradiation. Annealing conditions: high-temperature annealing above 1223 K with subsequent slow cooling (4–24 h) to ambient temperature; holding at 873 K for 12 h ($Ni_{52}Al_{48}$) and at 773 K for 12–120 h ($Ni_{50}Al_{50}$, $Ni_{52}Al_{48}$, $Ni_{55}Al_{45}$, $Ni_{60}Al_{40}$) during the cooling process. Irradiation conditions: $Ni_{49.5}Al_{50.5}$, electron energy $E_{e^-}=2.5$ MeV, electron dose $\Phi=1.0\times10^{23}$ m^{-2}; $Ni_{52}Al_{48}$, $E_{e^-}=2.9$ MeV, $\Phi=4.5\times10^{22}$ m^{-2}; $Ni_{60}Al_{40}$, $E_{e^-}=2.6$ MeV, $\Phi=1.0\times10^{23}$ m^{-2}.

competition with the quenched-in vacancies if the positron lifetimes in the two cases would differ.

3. Systematics of positron lifetimes in intermetallic compounds

The comparison of different states (i.e., after electron irradiation, quenching, or long-time annealing or in high-temperature thermal equilibrium) in the preceding sections (Secs. III A 1 and III A 2) enabled an assessment of the positron lifetimes in the free (τ_f) and in the vacancy-trapped state τ_1 in the various transition-metal aluminides. In the following, the systematics existing between the positron lifetimes in the various transition-metal aluminides are discussed by means of a comparison with the characteristic positron-lifetime values in the constituent pure metals (see Table I and Fig. 1). In addition, the positron-lifetime data for the intermetallic compounds NiZr or NiTi with group-IV and group-VIII transition-metal components are considered (Table I).

Although the free positron lifetime τ_f is determined by the details of the core and valence electron distribution as well as the positron wave function,[41] the averaged densities ρ_{el} of the outer s, p, and d electrons (cf. the valence electrons) may serve as a crude measure for τ_f. The increase of τ_f within the sequence Ni, Fe, Ti, Zr, and Al reflects the decrease of ρ_{el} (Table I, Fig. 1). The τ_f values in pure Ti and Zr observed in the present studies are similar to the values obtained earlier by Hood *et al.*[39] and are in agreement with the data of *ab initio* calculations.[23,40]

Based on the ρ_{el}-τ_f relationship, the following conclusions can be drawn with respect to the free positron lifetimes in the intermetallic compounds (Table I, Fig. 1).

(i) The similar positron lifetimes in the free state of the Ti-aluminides and of pure Ti are due to the rather similar electronic densities.

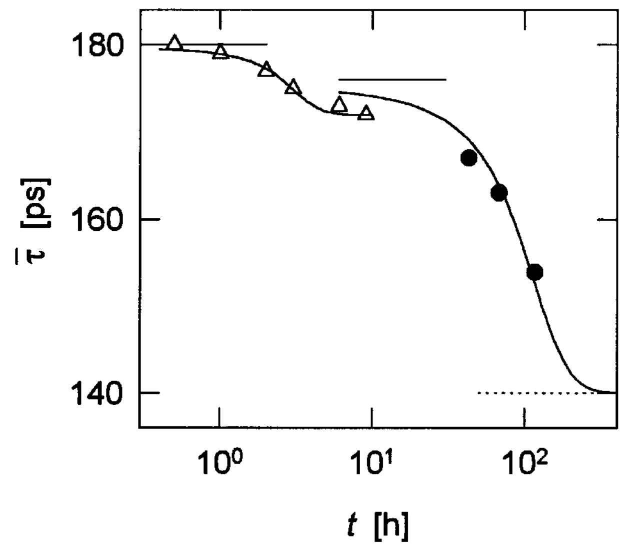

FIG. 4. Mean positron lifetime $\bar{\tau}$ measured at ambient temperature in $B2$-type $Fe_{61}Al_{39}$ after electron irradiation [electron energy $E_{e^-}=2.5$ MeV, electron dose $\Phi=9.1\times10^{22}$ m^{-2} (Δ); $E_{e^-}=2.6$ MeV, $\Phi=5.6\times10^{22}$ m^{-2} (●)] and subsequent isothermal annealing (time t) at $T_a=733$ K (Δ) or $T_a=633$ K (●). The solid lines denote fits [see Eq. (5) in Ref. 3] with the time constants $t_R=0.81$ h (733 K) or 42.3 h (633 K) for the annealing of vacancies. The positron lifetimes after long-time annealing (see Fig. 1) prior to irradiation (dotted line) and in the as-irradiated state (solid line) are depicted by horizontal lines.

(ii) In $Fe_{61}Al_{39}$, $Fe_{76.5}Al_{23.5}$, and Ni_3Al the free positron lifetimes τ_f are higher (i.e., by 6 ps, 7 ps, or 9 ps, respectively) than expected according to a linear interpolation of the τ_f values of the constituent pure metals Fe and Al or Ni and Al. As discussed earlier[2,42] this may be due to a charge transfer from the aluminum atoms to the transition-metal atoms.[43–46] This charge transfer gives rise to an enhancement of the positron wave function on the transition-metal sublattice and, therefore, to a shift of the τ_f values towards those of the transition metals.

(iii) For NiZr or NiTi, on the other hand, the τ_f values deviate only slightly from the interpolation between Ni and Zr or Ni and Ti, respectively. This indicates a more uniform distribution of the positron wave function within the two sublattices compared to the transition-metal aluminides.

(iv) For $B2$-NiAl where positron saturation trapping occurs due to the high concentrations of remnant vacancies (see Sec. III A 1) a free positron lifetime $\tau_f\simeq120$ ps similar as in FeAl is expected according to the ρ_{el}-τ_f relationship.

Regarding the positron lifetime $\tau_{1,\mathrm{irrad}}$ in the vacancy-trapped state after electron irradiation, the ratios $\tau_{1,\mathrm{irrad}}/\tau_f$ for the pure metals and the alloys (except for Zr and NiZr) studied in the present experiments (Fig. 1) fit the empirical relationship $\tau_1/\tau_f=1.5$–1.7 as observed for other metals.[47] In Zr and NiZr after irradiation and annealing at ambient temperature, the τ_1/τ_f ratio appears to be a little lower. This could indicate the formation of vacancy-impurity (e.g., vacancy-oxygen) complexes with a positron lifetime reduced in comparison to that of undecorated vacancies.[48]

B. Annealing behavior of irradiation-induced vacancies

In addition to a specific generation of vacancies for the assessment of positron lifetimes in intermetallic compounds (see Sec. III A), electron irradiation in combination with annealing studies provides information on the defect kinetics. For this purpose positron-lifetime measurements after electron irradiation and subsequent isothermal or isochronal annealing were performed on $Fe_{69}Al_{31}$ (Sec. III B 1) and on Ti-aluminides (Sec. III B 2).

1. Annealing of $Fe_{61}Al_{39}$ after electron irradiation

The increased mean positron lifetime $\overline{\tau}$ in electron-irradiated $Fe_{61}Al_{39}$ remains constant upon annealing at ambient temperature. From the variation of $\overline{\tau}$ during isothermal annealing at 623 K or 733 K (Fig. 4) time constants $t_R = 42.4$ h or 0.7 h, respectively, can be derived for the disappearance of irradiation-induced vacancies assuming a monomolecular reaction with homogeneously distributed sinks.[3] These time constants for the annealing process are in good agreement with the values 50.2 h (633 K) or 0.71 h (733 K) obtained for the equilibration of the thermal vacancy concentration at elevated temperatures with a vacancy migration enthalpy $H_V^M = 1.7$ eV (Ref. 3). The recovery in this temperature regime after electron irradiation which was also observed by means of electrical resistivity measurements[34] has, therefore, to be attributed to the migration of vacancies.

The high value of $\overline{\tau}$ after annealing at 773 K (Fig. 4) reflects the unique case that the annealing of irradiation-induced vacancies occurs at the very temperature where thermal vacancy formation can be detected by positrons. The final $\overline{\tau}$ value at 773 K is determined by the equilibrium concentration of vacancies[3] which is quenched in during subsequent cooling to ambient temperature. In contrast to the annealing of quenched-in vacancies (Sec. III A 1), however, no indication for vacancy agglomeration during annealing after electron irradiation was found. This is presumably due to the lower concentration of vacancies introduced by irradiation.

A few comments could be made regarding the microscopic mechanism of the recovery. The disappearance of radiation-induced Al vacancies may occur by conversion into Fe vacancies and Fe antisite atoms $(V_{\mathrm{Al}} \rightarrow V_{\mathrm{Fe}} + \mathrm{Fe}_{\mathrm{Al}})$. Such a process can occur at or below the temperature where the Fe vacancies become mobile and anneal out. It requires a nearest-neighbor jump of a Fe atom only and, furthermore, is associated with a gain of energy due to the higher formation enthalpy for vacancies on the Al sublattice compared to Fe vacancies.[37,49] For the same reasons, on the other hand, the probability of the opposite process, namely, the conversion of a Fe vacancy $(V_{\mathrm{Fe}} \rightarrow V_{\mathrm{Al}} + \mathrm{Al}_{\mathrm{Fe}})$, appears to be energetically unfavorable.

In the case of highly-iron-rich FeAl, the migration of Fe vacancies to sinks may exclusively occur via nearest-neighbor jumps of Fe atoms with Fe antisite atoms acting as bridges.[50]

2. Annealing of Ti-aluminides after electron irradiation

The main results of the annealing studies of the Ti-aluminides are as follows.

(a) After electron irradiation of $L1_0$-type $Ti_{48.5}Al_{51.5}$ and $D0_{19}$-type $Ti_{66.4}Al_{33.6}$ with low doses or energies of electrons a substantial decrease of the mean positron lifetime $\overline{\tau}$ upon annealing at ambient temperature is observed (Fig. 5, specimens Nos. C,D,E). In $Ti_{66.4}Al_{33.6}$ (specimen No. D) $\overline{\tau}$ decreases in a broad temperature range with substages at ~230 K and ~450 K.

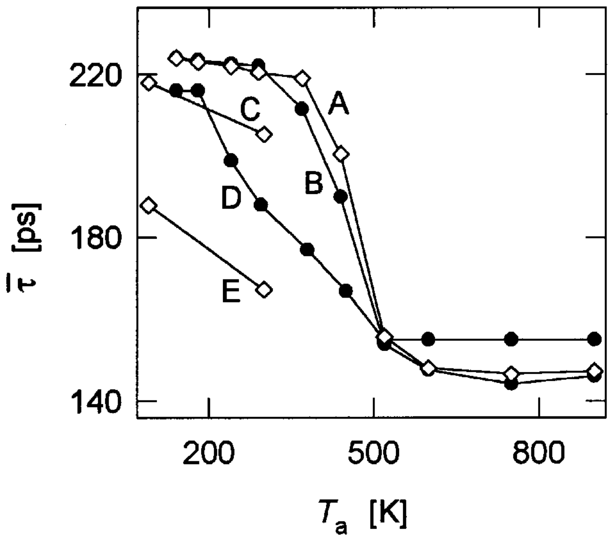

FIG. 5. Mean positron lifetime $\overline{\tau}$ in $L1_2$-type $Ti_{48.5}Al_{51.5}$ (◇) and $D0_{19}$-type $Ti_{65.6}Al_{34.4}$ (●) after electron irradiation and subsequent isochronal annealing at the temperature T_a (annealing time t = 30 min). Electron energy $E_{e^-} = 2.5$ MeV, electron dose $\Phi = 1.1 \times 10^{23}$ m^{-2} (A,B); $E_{e^-} = 2.5$ MeV, $\Phi = 5 \times 10^{22}$ m^{-2} (C); $E_{e^-} = 2.6$ MeV, $\Phi = 2.1 \times 10^{22}$ m^{-2} (D); $E_{e^-} = 0.55$ MeV, $\Phi = 1 \times 10^{23}$ m^{-2} (E).

(b) After high-dose irradiation only the second recovery stage centered at ~450 K ($Ti_{66.4}Al_{33.6}$) or at slightly higher temperatures (~480 K, $Ti_{48.5}Al_{51.5}$; see Fig. 4) is observed due to saturation trapping of positrons at vacancies at lower annealing temperatures.

(c) The positron lifetime $\tau_1 = 220$–223 ps due to trapping at irradiation-induced vacancies remains constant throughout the course of annealing for each of the present specimens (Nos. A–E).

The $\overline{\tau}$ variation upon annealing found here is in agreement with results obtained by Shirai and Yamaguchi for $Ti_{75}Al_{25}$ (Ref. 51) and $Ti_{44}Al_{56}$ (Ref. 52). The rather similar annealing behavior in $D0_{19}$-Ti_3Al and $L1_0$-TiAl [items (a) and (b)] may reflect the similar coordination numbers and nearest-neighbor distances of the two crystal structures. From item (c) we conclude that vacancies migrate in the annealing stage at ~450 K and disappear without the formation of vacancy agglomerates.

In the $D0_{19}$-type lattice ($Ti_{66.4}Al_{33.6}$) the irradiation-induced vacancies on the Al sublattice presumably convert into vacancies on the Ti sublattice during annealing similarly as assumed in the case of Fe-rich FeAl (see Sec. III B 1). This follows from the distance $d = 0.406$ nm required for Al-Al jumps within the Al sublattice in comparison to the closer distance ($d = 0.285$ nm and 0.290 nm) associated with nearest-neighbor jumps between the two sublattices ($d = 0.285$ nm and 0.290 nm).

In $L1_0$-type $Ti_{48.5}Al_{51.5}$ with a layered stacking of {100} Ti and Al planes, on the other hand, Al and Ti vacancies can migrate by means of nearest-neighbor atomic jumps both within their own sublattice (nearest-neighbor distance $d = 0.282$ nm) and between the two sublattices ($d = 0.287$ nm). The former migration route would be confined to two dimensions. Indications for an anisotropic migration behavior of defects in $L1_0$-type TiAl compared to $D0_{19}$-type Ti_3Al were deduced from the observation of different cluster densities by means of transmission electron microscopy after He-ion[53] or high-dose electron irradiation.[54]

The present results on defect annealing with the interpretation of the 450 K stage in terms of vacancy migration may be compared with studies of the self-diffusion and the thermal vacancy formation. Applying a simple relationship

$$H_V^M = Q^{SD} - H_V^F \tag{3}$$

for a vacancy-mediated self-diffusion process, vacancy migration enthalpies $H_V^M = 1.59$ eV (TiAl) or 1.45 eV (Ti_3Al) are estimated from the activation enthalpy $Q^{SD} = 3$ eV [TiAl (Ref. 55), Ti_3Al (Ref. 56)] for the ^{44}Ti self-diffusion and the vacancy formation enthalpies $H_V^F = 1.4$ eV [TiAl (Ref. 4)] or 1.55 eV [Ti_3Al (Ref. 5)]. A slightly lower value $H_V^M = 1.2$ eV follows from a calculation of atomic jump rates for an annealing process at 450 K assuming a mean number of 10^4 jumps per vacancy to sinks and a vacancy migration entropy $S_V^M = 1 k_B$ [see Eq. (8) in Ref. 3]. Within the experimental uncertainties and taking into account the fact that the simple relationship (3) may be considered at the most as an estimate in the case of intermetallic compounds, the H_V^M values deduced at low and high temperatures may still be compatible. From the annealing stage at 250 K, however, an activation enthalpy considerably below the vacancy migration enthalpy estimated above is suggested. This stage, therefore, can hardly be attributed to vacancy migration but rather might be due to the recombination of vacancies with migrating interstitial atoms.

IV. SUMMARY

The main results of the comparative vacancy studies in intermetallic compounds after electron irradiation may be summarized as follows.

(i) In $B2$-type Fe- and Ni-aluminides usual cooling conditions after high-temperature processing gives rise to a supersaturation of thermal vacancies due to low vacancy diffusivities.

(ii) The identical τ_1 values in vacancies induced by irradiation with different electron energies (Ni_3Al, TiAl) or present in the as-prepared state ($B2$-type aluminides) indicate similar positron lifetimes in the vacancies of the different sublattices. The positron lifetimes experimentally observed in the vacancy-trapped state of the various intermetallic compounds support the available results of positron-lifetime calculations.

(iii) The characteristics of the positron lifetimes in the free and vacancy-trapped states of the intermetallic compounds can be correlated to a great extent to the corresponding values in the constituent pure metals. For a more profound assessment of this correlation further calculations of positron lifetimes in intermetallic compounds would be desirable.

(iv) The annealing of irradiation-induced vacancies in $Fe_{61}Al_{39}$ occurs with the same time constants as the equilibration of the thermal vacancy concentration.

(v) The migration of vacancies in Ti aluminides as concluded from the annealing behavior after irradiation occurs at temperatures $T_a \simeq 450$ K slightly lower than expected from self-diffusion and thermal vacancy formation.

(vi) A microscopic consideration of the atomic jump mechanisms suggests that in $B2$-FeAl and $D0_{19}$-Ti_3Al vacancies on the Al sublattice convert into Fe vacancies during migration. A more detailed assessment of these processes, which is also essential for the self-diffusion, demands for a theoretical simulation and understanding of the atomic jump mechanisms.

ACKNOWLEDGMENTS

The authors are indebted to U. Kneissl (Dynamitron accelerator of Stuttgart University) for fruitful collaboration and discussion, to B. Fischer, H. Hollick (Dynamitron accelerator of Stuttgart University), and L. Raschke (MPI f. Metallforschung, Stuttgart) for technical assistance, to P.A. Beaven (GKSS, Geesthacht, Germany), T. Gödecke (MPI f. Werkstoffwissenschaften, Stuttgart), H. Wever, F. Zobel, Y. Shi (TU Berlin), G. Frommeyer, G. Sauthoff, and U. Reimann (MPI f. Eisenforschung, Düsseldorf) for the specimen material as well as to Y. Shirai for making available experimental results prior to publication. The continuous interest of A. Seeger and the financial support of the Deutsche Forschungsgemeinschaft (Grant Nos. Scha428/12-1 and Scha428/17-2) are appreciated.

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[1] H.-E. Schaefer, Phys. Status Solidi A **102**, 47 (1987).

[2] H.-E. Schaefer, R. Würschum, M. Šob, T. Žák, W. Yu, W. Eckert, and F. Banhart, Phys. Rev. B **41**, 11 869 (1990).

[3] R. Würschum, C. Grupp, and H.-E. Schaefer, Phys. Rev. Lett. **75**, 97 (1995).

[4] U. Brossmann, R. Würschum, K. Badura, and H.-E. Schaefer, Phys. Rev. B **49**, 6457 (1994).

[5] R. Würschum, E. Kümmerle, K. Badura-Gergen, A. Seeger, Ch. Herzig, and H.-E. Schaefer, J. Appl. Phys. (to be published).

[6] H.-E. Schaefer, R. Würschum, and J. Bub, Mater. Sci. Forum **105-110**, 439 (1992).

[7] K. Badura, U. Brossmann, R. Würschum, and H.-E. Schaefer, Mater. Sci. Forum **175-178**, 295 (1995).

[8] K. Badura-Gergen, Ph.D. thesis, Universität Stuttgart, 1995.

[9] R. Würschum, T. Troev, and B. Grushko, Phys. Rev. B **52**, 6411 (1995).

[10] R. Würschum, B. Grushko, K. Urban, and H.-E. Schaefer, Philos. Mag. B **70**, 913 (1994).

[11] R. Würschum, M. Rollinger, H. Kisker, A. Raichle, B. Damson, and H.-E. Schaefer, Nanostruct. Mater. **6**, 377 (1995).

[12] R. Würschum, W. Bauer, K. Maier, A. Seeger, and H.-E. Schaefer, J. Phys. Condens. Matter **1**, SA33 (1989).

[13] A.A. Rempel and H.-E. Schaefer, Appl. Phys. A **61**, 51 (1995).

[14] *Positrons in Solids*, edited by P. Hautojärvi (Springer, Berlin, 1979).

[15] A. Seeger, Appl. Phys. **4**, 183 (1974).

[16] R. Würschum and H.-E. Schaefer, Phys. Status Solidi A **103**, 101 (1987).

[17] M. J. Puska (private communication).

[18] T.-M. Wang, M. Shimotomai, and M. Doyama, J. Phys. F **14**, 37 (1984).

[19] Y. Jirásková, O. Schneeweiss, and M. Šob, Mater. Sci. Forum **175-178**, 399 (1995).

[20] E.A. Kümmerle, K. Badura, B. Sepiol, H. Mehrer, and H.-E. Schaefer, Phys. Rev. B **52**, 6947 (1995).

[21] R. Würschum, P. Donner, E. Hornbogen, and H.-E. Schaefer, Mater. Sci. Forum **105-110**, 1333 (1991).

[22] R. Würschum, W. Greiner, R.Z. Valiev, M. Rapp, W. Sigle, O. Schneeweiss, and H.-E. Schaefer, Scr. Metall. Mater. **25**, 2451 (1991).

[23] M.J. Puska, J. Phys. Condens. Matter **3**, 3455 (1991).

[24] H.-E. Schaefer and R. Würschum, Phys. Lett. A **119**, 370 (1987).

[25] A. Vehanen, P. Hautojärvi, J. Johansson, J. Yli-Kauppila, and P. Moser, Phys. Rev. B **25**, 762 (1982).

[26] Y. Shirai, H.-E. Schaefer, and A. Seeger, in *Positron Annihilation*, edited by L. Dorikens-Vanpraet, M. Dorikens, and D. Segers (World Scientific, Singapore, 1989), p. 419.

[27] M.J. Puska and R.M. Nieminen, J. Phys. F **13**, 333 (1983).

[28] M. Franz, J.-E. Kluin, D. Schmid, and Th. Hehenkamp, Verh. Dtsch. Phys. Ges. VI **26**, 1284 (1991).

[29] H.-E. Schaefer, R. Gugelmeier, M. Schmolz, and A. Seeger, Mater. Sci. Forum **15-18**, 111 (1987).

[30] K. Badura and H.-E. Schaefer, Z. Metallkd. **84**, 405 (1993).

[31] A. J. Bradley and A. Taylor, Proc. R. Soc. London A **159**, 62 (1937).

[32] J.P. Rivière and J. Grilhé, Scr. Metall. **9**, 967 (1975).

[33] J.P. Rivière and J. Grilhé, Phys. Status Solidi A **25**, 429 (1974).

[34] J.P. Rivière, J.F. Dinhut, and J. Dural, Radiat. Eff. **69**, 47 (1983).

[35] F. Zobel, Ph.D. thesis, Technische Universität Berlin, 1994.

[36] G.F. Hancock and B.R. McDonnell, Phys. Status Solidi A **4**, 143 (1971).

[37] C.L. Fu, Y.-Y. Ye, M.H. Yoo, and K.M. Ho, Phys. Rev. B **48**, 6712 (1993).

[38] O. Dimitrov and C. Dimitrov, Intermetallics **2**, 249 (1994).

[39] G.M. Hood, M. Eldrup, and N.J. Pedersen, in *Positron Annihilation*, edited by R.R. Hasiguti and K. Fujiwara (Japan. Institute of Metals, Sendai, 1979), p. 751.

[40] K.O. Jensen, J. Phys. Condens. Matter **1**, 10 595 (1989).

[41] R.M. Nieminen and M.J. Manninen, in *Positrons in Solids*, edited by P. Hautojärvi (Springer, Berlin, 1979), p. 145.

[42] M. Šob, H.-E. Schaefer, and R. Würschum, Mat. Fiz. Astron. LIX **1342**, 161 (1991).

[43] C. Müller, H. Wonn, W. Blau, P. Ziesche, and V.P. Krivitskii, Phys. Status Solidi B **95**, 215 (1979).

[44] W. Hoppe, U. Marx, G. Dlubek, and O. Brümmer, Cryst. Res. Technol. **23**, 393 (1988).

[45] S. Ishida, J. Ishida, S. Asano, and J. Yamashita, J. Phys. Soc. Jpn. **41**, 1570 (1976).

[46] C.L. Fu and M.H. Yoo, Acta Metall. Mater. **40**, 703 (1992).

[47] A. Seeger and F. Banhart, Phys. Status Solidi A **102**, 171 (1987).

[48] H.E. Hansen, R.M. Nieminen, and M.J. Puska, J. Phys. F **14**, 1299 (1984).

[49] J. Mayer, C. Elsässer, and M. Fähnle, Phys. Status Solidi B **191**, 283 (1995).

[50] C.R. Kao and Y.A. Chang, Intermetallics **1**, 237 (1993).

[51] Y. Shirai (private communication).

[52] Y. Shirai and M. Yamaguchi, Mater. Sci. Eng. A **152**, 1731 (1992).

[53] K. Nakata, K. Fukai, A. Hishinuma, K. Aneyama, and M. Tokziane, J. Nucl. Mater. **202**, 39 (1993).

[54] A. Hishinuma, K. Nakata, K. Fukai, K. Aneyama, and M. Tokziane, J. Nucl. Mater. **199**, 167 (1993).

[55] S. Kroll, N. A. Stolwijk, R. Rosenkranz, C. Herzig, and H. Mehrer, Z. Metallkd. **83**, 591 (1992).

[56] J. Rüsing and C. Herzig, Scr. Metall. Mater. **33**, 561 (1995).