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Thermal vacancies and positron-lifetime measurements in $Fe_{76.3}Al_{23.7}$

H.-E. Schaefer and R. Würschum
Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Postfach 80 11 40, D-7000 Stuttgart 80, Federal Republic of Germany

M. Šob and T. Žák
Institute of Metallurgy, Czechoslovak Academy of Sciences, Žižkova 22, CS-61662 Brno, Czechoslovakia

W. Z. Yu
Department of Physics, Qinghua University, Beijing 100 084, People's Republic of China

W. Eckert
Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Postfach 80 11 40, D-7000 Stuttgart 80, Federal Republic of Germany

F. Banhart
Institut für Physik, Max-Planck-Institut für Metallforschung, D-7000 Stuttgart 80, Federal Republic of Germany

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The formation of thermal vacancies in the intermetallic compound $Fe_{76.3}Al_{23.7}$ was investigated between 20 and 1060 °C by positron-lifetime measurements. The positron lifetime $\tau_f = 112$ ps at 20 °C indicates that no structural vacancies can be detected. The increase of the mean positron lifetime $\bar{\tau}$ due to thermal vacancy formation starts at relatively low temperatures ($T_3 = 475\,^\circ\mathrm{C}$). The fit of a simple two-state trapping model to the temperature variation of $\bar{\tau}$ yields an effective vacancy formation enthalpy $H^F = 1.18 \pm 0.04$ eV, which suggests a thermal vacancy concentration at the melting temperature of several atomic percent which is much higher than in pure metals and similar to that found in some intermetallic compounds with a $B2$ structure. From a comparison with self-diffusion results, a vacancy migration enthalpy of $H^M = 1.4-1.6$ eV is deduced. The phase transitions in the present alloy are discussed in terms of vacancy formation and migration.

I. INTRODUCTION

Intermetallic compounds are considered as future high-temperature structural materials. For high-temperature and material transport properties the formation of thermal equilibrium defects such as vacancies is of particular importance because many diffusion processes are controlled by thermally formed vacancies. Vacancy concentrations of several atomic percent (much higher than in pure metals) have been observed under high-temperature thermal equilibrium conditions in ordered intermetallic compounds of group-VIIIA transition metals and group-IIIB metals with CsCl ($B2$) structure, e.g., in NiGa,[1,2] CoGa,[3,4] or FeAl (Ref. 5) (for an overview, see Ref. 6). In the case of iron-rich Fe-Al alloys, their prospects as soft magnetic materials are of additional interest. From the point of view of solid-state physics the vicinity of the Fe_3Al composition attracts special attention because of the variety of structural phase transitions (see Fig. 1) between the low-temperature ordered DO_3 structure, the partially disordered $B2$ structure, the disordered high-temperature $A2$ structure, and the two-phase regions at intermediate temperatures.

Positron annihilation[8] and in particular positron lifetime spectroscopy[9] have proved to be most powerful

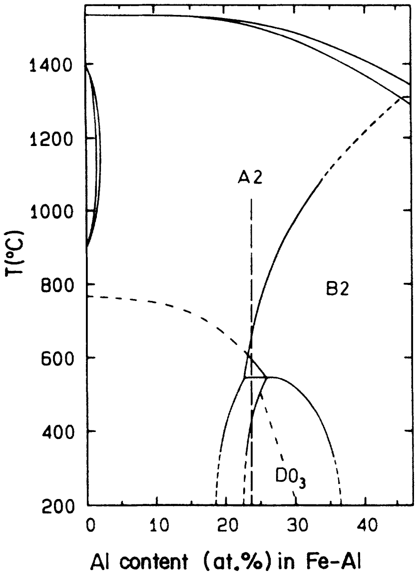

FIG. 1. Phase diagram of the Fe-Al system in the vicinity of Fe_3Al (Ref. 7). The composition of the present specimen and the magnetic order-disorder transitions (—·—·—·) are indicated.

techniques for studying the thermal equilibrium vacancy concentration at high temperatures in pure metals. They also have been applied to vacancy formation studies in semiconductors[10] and metal oxides.[11] Only a few high-temperature positron-annihilation measurements on intermetallic compounds, e.g., NiAl, FeAl (Ref. 12) or CuAu,[13,14] Cu_3Au,[14,15] and CuZn (Refs. 16 and 17) were reported.

In the simplest case of the applicability of a two-state positron trapping model,[18] the positron trapping rate σC_{1V} at thermally formed monovacancies, with the atomic concentration C_{1V} and the specific positron trapping rate σ, is given by

$$\sigma C_{1V}=\frac{1}{\tau_f}\frac{\bar{\tau}-\tau_f}{\tau_1-\bar{\tau}}=I_1\left[\frac{1}{\tau_0}-\frac{1}{\tau_1}\right] . \tag{1}$$

Here, τ_f is the "free" positron lifetime in the defect free crystal, τ_1 that in the vacancy state, and $\bar{\tau}$ the mean positron lifetime. The time constants $\tau_0=[(1/\tau_f)+\sigma C_{1V}]^{-1}$ and τ_1 as well as the relative intensity I_1 can be determined from the numerical analyses[19,20] of the measured positron lifetime spectra. Assuming a temperature-independent σ, the activation enthalpy H_{1V}^F for monovacancy formation can be directly derived from the temperature variation of σC_{1V} [Eq. (1)] with

$$C_{1V}=\exp\left[\frac{S_{1V}^F}{k_B}\right]\exp\left[\frac{-H_{1V}^F}{k_B T}\right] , \tag{2}$$

where S_{1V}^F designates the monovacancy formation entropy. Assuming a value $\sigma=4\times10^{14}\ s^{-1}$, similar to that which was obtained for high-purity Al or Au,[9] absolute values of the vacancy concentration can be estimated from the trapping rates determined according to Eq. (1).

In pure metals, the lifetime of a positron in a trap may be used for the characterization of the type of trap as monovacancies, divacancies, etc.,[21] or larger free volumes.[22] The temperature variation of the positron trapping rate σC_{1V} was extensively used for the determination of vacancy formation enthalpies (see Ref. 9).

In binary alloys, however, the positron lifetime τ_f in the free delocalized state may yield information on which sublattice the positrons are predominantly annihilated. From the value of the positron lifetime measured at temperatures far below thermal vacancy formation, it may be, in addition, assessed whether structural vacancies are present in the alloy.

It should be pointed out that the apparent vacancy formation enthalpy determined in intermetallic compounds according to the simple model of Eq. (1) has to be considered as an effective quantity for three reasons:

(i) Particularly in group-VIII*A*–group-III*B* compounds, the process of thermal defect formation comprises vacancies in high concentration *and* the generation of antisite defects.[4,12,23] This may give rise to a variation of the apparent formation enthalpy with temperature and composition.[4]

(ii) At elevated vacancy concentrations, multiple vacancies, e.g., divacancies,[9,24] are expected to contribute to positron trapping in addition to monovacancies, and should be taken into account in the analyses.

(iii) As in the present case of an alloy near Fe_3Al, the temperature range where vacancy formation can be detected sensitively by positron trapping may be extended over various phase regions with different vacancy formation properties.

II. EXPERIMENTAL PROCEDURES

The $Fe_{76.3}Al_{23.7}$ alloy was prepared by melting carbonyl iron (carbon content below 0.01 at. %) and aluminum of 99.999% purity in an induction furnace under an argon atmosphere with subsequent casting of the ingot in a copper mold. For the positron lifetime measurements, a cylindrical specimen (13 mm in length, 3 mm in diameter) with an axial bore hole (10 mm in depth, 1 mm in diameter) and a cover were machined and chemically etched in a solution of 6% HF, 69% H_2O_2, and 25% H_2O. After deposition of the positron emitter (6×10^5 Bq of $^{22}NaCl$) in the bore hole, the specimen was sealed by electron-beam welding.[25] For the measurements between 20 and 1060 °C, the specimen was encapsulated in a quartz vial under high vacuum and heated in a narrow resistance-heated furnace (outer diameter 16 mm) with temperature control within $\pm0.5\,°C$. The lifetime spectra were taken with a total number of $0.6-1.7\times10^6$ coincidence counts by means of a fast-slow time spectrometer with Pilot U scintillators yielding a time resolution of full width at half maximum (FWHM)=330 ps. After subtraction of a temperature-independent source component (intensity $I_s=4\%$, time constant $\tau_s=320$ ps), the spectra were evaluated by means of two-component analyses.[19,20]

III. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 2 the temperature variation of the mean positron lifetime $\bar{\tau}=I_0\tau_0+I_1\tau_1$ is shown for three out of five successive runs performed with increasing or decreasing temperature. All the data coincide within experimental

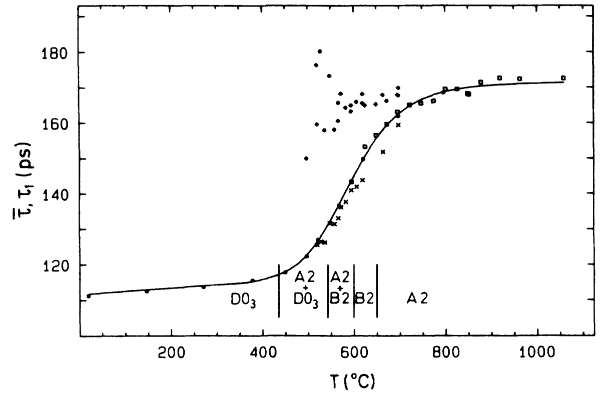

FIG. 2. Temperature variation of the mean positron lifetime $\bar{\tau}=I_0\tau+I_1\tau_1$ for measuring runs no. 1 (●), no. 3 (×), and no. 5 (□). Within experimental uncertainty the same temperature variation of $\bar{\tau}$ is observed in all measuring runs except in run no. 3. In addition, the time constant τ_1 (♦) as derived from two-component analyses is plotted. The solid line shows a fit of the simple two-state trapping model to the experimental data (without run no. 3) yielding the parameters given in Eq. (3).

uncertainty except run no. 3, which deviates a little, but not in the direction which is expected for a hysteresis behavior. Starting from $\bar{\tau}=112$ ps at 20 °C an S-shaped increase, as typical for positron trapping and annihilation at thermally formed vacancies in pure metals,[9] is observed between 450 and 800 °C with some tendency to saturation at higher temperatures. The linear temperature variation of $\tau_f(T)=\tau_{f0}(1+\alpha T)$ between 20 and 400 °C yields $\alpha=0.91\times10^{-4}$ K^{-1}, which appears to be slightly smaller than in α-Fe.[9]

The room-temperature value of $\bar{\tau}=\tau_f=112$ ps is rather similar to the low values in transition metals,[9] and strongly indicates that this is the positron lifetime in a delocalized state and that no positron trapping occurs. Obviously the atomic concentration of structural vacancies in this alloy lies below the detection limit ($\sim10^{-6}$) for positrons. The possibility of measuring the absolute values of positron lifetimes as fingerprints for various positron states favors this technique for the detection of structural vacancies over the measurements of Doppler broadening (DB) or angular correlation of the annihilation radiation.

From the value of the free positron lifetime $\tau_f=112$ ps, we expect some information on which sublattice the positrons are annihilated. At first sight, this value, which is slightly higher than that in α-Fe [$\tau_f=106$ ps (Ref. 26)], suggests predominant annihilation on the Fe-sublattice. For a detailed consideration, however, the electron density distribution should be considered. By incorporation of the Al atom into the bcc-type lattice of $\mathrm{Fe_3Al}$, its atomic volume is substantially reduced (by about 30%) in comparison to pure Al which may be due to a strong charge transfer from Al to Fe. The latter point is supported by electronic band-structure calculations. Taking the APW results of Ishida *et al.*[27] for the $\mathrm{D0_3}$-ordered $\mathrm{Fe_3Al}$ system, and supposing that the electrons outside the muffin-tin spheres may be added proportionally to the electrons inside the muffin-tin spheres, one finds that the Al atoms lose 1.00 electrons and the Fe II atoms [with four Fe and four Al atoms as nearest neighbors (see Fig. 3)] each gain 0.57 electrons. An additional slight charge transfer (0.14 electrons) is expected from the Fe I atoms (eight nearest-neighbor Fe atoms) to the Fe II atoms. A similarly strong charge transfer from the Al atoms is expected to occur in FeAl (Ref. 28). From this electron density pattern suggested for $\mathrm{Fe_3Al}$ the positron wave function is expected to be concentrated on the Fe sublattice and repelled from the positively charged Al sublattice. This behavior would be different from that of protons, which are expected to be localized on octahedral sites neighbouring Al Atoms.[29] The measured value of the free positron lifetime $\tau_f=112$ ps fits best to the electron density at the Fe I atoms slightly reduced to that in pure α-Fe. This τ_f value may indicate that annihilation of positrons near the Fe II sites is less likely because the high electron density there is expected to give rise to τ_f values lower than those determined experimentally. This would be in contrast to the expectation that positrons assume the lowest total energy on lattice sites of maximum density of negative charge.[30]

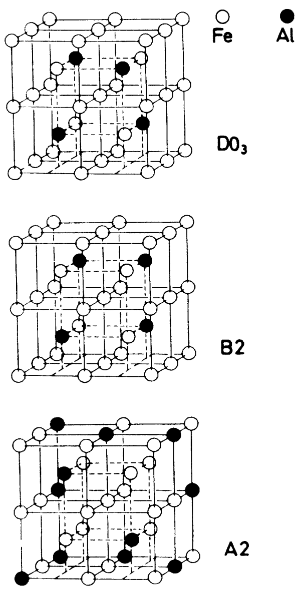

FIG. 3. Structure types occuring in the $\mathrm{Fe_{76.3}Al_{23.7}}$ alloy. In the text the primitive cubic lattices of the central (— — —) or the cube edge (—) atoms are designated by A and B, respectively.

For the discussion of thermal vacancy formation as detected by the positron lifetime measurements in the present alloy, we first want to point out that trapping starts to occur at $T_t=475$ °C. This is, relative to the solidus-liquidus temperature $T_M=1500$ °C of this alloy, much lower (ratio of the absolute temperatures $T_t/T_M=0.42$) than in the case of pure bcc iron[26] and fcc metals ($T_t/T_M=0.6$) or pure bcc metals ($T_t/T_M=0.68$).[9,25] This suggests a rather high concentration level of thermal vacancies in the present alloy if the specific trapping rate $\sigma=4\times10^{14}$ s^{-1} applies. This value of σ appears to be reasonable also for alloys, because from the positron trapping rate σC_{1V} in quenched $\mathrm{Ni_3Al}$ (Ref. 31) and calculations of the thermal equilibrium concentration C_{1V} in $\mathrm{Ni_3Al}$ (Ref. 32) a rather similar value of $\sigma=3.9\times10^{14}$ s^{-1} can be derived.

A fit of the simple two-state trapping model according to Eqs. (1) and (2) to the total set of data in Fig. 2 yields the apparent enthalpy of vacancy formation

$$H^F=1.18\pm0.04\ \mathrm{eV}\ , \tag{3a}$$

together with

$$\sigma\exp\left[\frac{S^F}{k_B}\right]=6.1\times10^{16}\ \mathrm{s}^{-1} \tag{3b}$$

and

$$\tau_1=171\pm1\ \mathrm{ps}\ . \tag{3c}$$

Similar values of H^F and $\sigma\exp(S^F/k_B)$ result from an Arrhenius plot of the positron trapping rate $\sigma C_{1V}=I_1(1/\tau_0-1/\tau_1)$ between 500 and 630 °C with the parameters τ_0, τ_1, and I_1 as deduced from a two-component fit of the positron lifetime spectra. The fit of the simple two-state trapping model to the $\bar{\tau}$ data in Fig. 2 is not fully satisfying and the value of $\tau_1 = 171$ ps from this fit is significantly higher than the values ($\tau_1 \approx 165$ ps) derived from two-component analyses of the spectra measured just above T_t. This fit to the $\bar{\tau}$ data becomes even worse if a fixed value of $\tau_1 = 165$ ps is used. We therefore tested two extended models including either divacancy formation[9] or a temperature-dependent monovacancy formation enthalpy[33] and shall present in the following the results in a concise survey.

A model including divacancies for the interpretation of the data requires a rather high divacancy binding energy $H^B_{2V} \approx 0.6$ eV and invokes a unrealistically high divacancy concentration $C_{2V}(T_M) \gtrsim 1.0$. We therefore think that the slight deviations from the simple model cannot be ascribed to a detectable contribution of divacancies in the present temperature range. They may be due to a weak temperature variation of the positron lifetime in thermally formed vacancies. However, for investigating the clustering of thermal vacancies, measurements to even higher temperatures are desirable.

In order to consider a temperature-dependent vacancy formation enthalpy, the linear relationship[33]

$$H^F(T) = H^F(T_0) + \alpha^F k_B (T - T_0) \tag{4}$$

is used, where we choose $T_0 = 600\,^{\circ}\mathrm{C}$ at the center of the S curve (Fig. 2). From a fit of Eqs. (1), (2), and (4) to the data in Fig. 2 a value of $\alpha^F = 1.0 \pm 1.0$ can be derived with $H^F(T_0) = 1.17 \pm 0.03$ eV. This value of α^F differs strongly from the value $\alpha^F = -5.3$, which can be derived from the data of van Ommen *et al.*[4] for Co-rich CoGa, and which may reflect a relatively complex thermal equilibrium defect pattern of vacancies and antisite defects.[4] The above value of $\alpha^F = 1.0 \pm 1.0$, which is similar to that expected for pure metals, may therefore indicate for $\mathrm{Fe}_{76.3}\mathrm{Al}_{23.7}$ the formation of a more simple defect pattern with mainly monovacancies.

For a discussion of some general features of our results we may make use of the data set given by Eq. (3). The apparent vacancy formation entropy as derived from Eq. (3b) with $\sigma = 4 \times 10^{14}\ \mathrm{s}^{-1}$ assumes a relatively high value $S^F = 5k_B$. The apparent vacancy formation enthalpy is, in relation to the melting temperature T_M, rather low ($H^F/k_B T_M = 7.7$) compared to pure fcc metals ($H^F_{1V}/k_B T_M = 8.1$) or bcc metals ($H^F_{1V}/k_B T_M = 11.2$).[25] In comparison to that we should mention that rather low apparent vacancy formation enthalpies of about 0.8 eV can be derived for the iron-rich $B2$ phases of FeAl.[5,34] Approaches for interpreting the temperature variation of the thermal equilibrium defect concentrations and of the apparent formation enthalpies in terms of vacancy and antisite defect formation on the two sublattices were presented by Bakker and van Ommen,[35] van Ommen *et al.*,[4] and Kim[12,32] for ordered $B2$ and $L1_2$ ($\mathrm{Cu_3Au}$) structures starting from nearest-neighbor bond energy models. A theoretical treatment of the temperature-dependent thermal vacancy concentration as detected in the present alloy by positron lifetime measurements is still more complex because of the occurrence of ordered phases, disordered phases, and two-phase regions.

According to the presently determined values of H^F and S^F, the vacancy equilibrium concentrations at the phase transitions[7,36] of the present alloy exhibit the following values:

$$C^{\mathrm{eq}}_{1V}(435\,^{\circ}\mathrm{C}) = 5.9 \times 10^{-7}\ , \tag{5a}$$

$$C^{\mathrm{eq}}_{1V}(543\,^{\circ}\mathrm{C}) = 7.6 \times 10^{-6}\ , \tag{5b}$$

$$C^{\mathrm{eq}}_{1V}(600\,^{\circ}\mathrm{C}) = 2.3 \times 10^{-5}\ , \tag{5c}$$

$$C^{\mathrm{eq}}_{1V}(645\,^{\circ}\mathrm{C}) = 4.9 \times 10^{-5}\ , \tag{5d}$$

$$C^{\mathrm{eq}}_{1V}(T_M = 1500\,^{\circ}\mathrm{C}) = 6.6 \times 10^{-2}\ . \tag{5e}$$

This shows that vacancies are present in measurable concentrations at relatively low temperatures. At the melting temperature T_M the vacancy concentration is higher by a factor of 100 than in most high-purity metals and exhibits similarly high values as in the ordered $B2$ phases of group-*VIII A*–group-*IIIB* intermetallic compounds.[1–5] Assuming higher values of σ and lower values of S^F in Eq. (3b), within reasonable limits, would yield vacancy concentrations lower by a factor of 20 at most.

In the following we now will discuss the question which lattice sites, Al or Fe sites, the thermally formed vacancies actually occupy. The similarity of the positron lifetime $\tau_1 = 171$ ps of vacancies in $\mathrm{Fe}_{76.3}\mathrm{Al}_{23.7}$ to that in electron-irradiated α-Fe [$\tau_{1V} = 175$ ps (Ref. 37)] is rather understandable. On the one hand, the lattice constants in both crystals and therefore the sizes of unrelaxed monovacancies differ only slightly. In addition, vacancies both on Al and on Fe I sites in the alloy are fully surrounded by Fe nearest neighbors, such as in α-Fe. Therefore, in the present case, we expect the vacancies on the both sites to be barely distinguishable by positron lifetime measurements.

The high vacancy concentrations in the ordered intermetallic $B2$ compounds at elevated temperatures[1–5] are ascribed to the formation of the so-called triple defect,[1,4] and there is experimental evidence[1,38] that the vacancies are predominantly located on the group-VIII*A* (e.g., Fe) sublattice. Also in $\mathrm{Ni_3Al}$ with its $L1_2$ ($\mathrm{Cu_3Au}$) structure, theoretical studies[32] indicate that thermal vacancies are formed mainly on the Ni sublattice, which is due to the lower total energy of the vacancies on these sites. In this picture the enthalpy for vacancy formation on the Al sublattice exceeds the value characteristic for the transition-metal sublattice. As concluded from this evidence, it is plausible that in the alloys near the $\mathrm{Fe_3Al}$ composition, as studied in the present work, vacancies are located on the Fe I or the Fe II sites. More information may be obtained from further studies of $\bar{\tau}(T)$ at stoichiometries above and below the stoichiometric $\mathrm{Fe_3Al}$ compound.

For an estimate of the vacancy migration enthalpy H^M in $\mathrm{Fe}_{76.3}\mathrm{Al}_{23.7}$, the presently determined apparent formation enthalpy H^F may be compared to the results of self-diffusion studies. For the Al self-diffusivity in Fe_3Al between 900 and 1100 °C, the relationship

$$D_{Al}=100\exp\left[\frac{-2.76\ \mathrm{eV}}{k_BT}\right]\ \mathrm{cm^2\,s^{-1}} \tag{6a}$$

and for the Fe self-diffusivity between 927 and 1154 °C

$$D_{Fe}=3.2\exp\left[\frac{-2.6\ \mathrm{eV}}{k_BT}\right]\ \mathrm{cm^2\,s^{-1}} \tag{6b}$$

were reported.[39]

Assuming simple self-diffusion mechanisms, governed by monovacancy formation and migration, and making use of the H^F value given in Eq. (3a), a relatively high value of $H^M=1.4-1.6$ eV is obtained for the temperature range of the disordered $A2$ phase. Similar values of 1.3 eV (Ref. 40), 1.57 eV (Ref. 41), or ~1.41 eV (Ref. 34) were reported after quenching of $Fe_{75.6}Al_{24.4}$, $Fe_{61.5}Al_{38.5}$, or $Fe_{60}Al_{40}$, respectively. As a consequence, a ratio $H^M/H^F>1$, higher than in pure metals, is obtained. This means that even at elevated thermal vacancy concentrations their migration is rather slow. Therefore, direct measurement of the vacancy migration enthalpy is expected to be possible over a wide temperature range by studying the time-dependent approach to the vacancy equilibrium concentration in fast temperature-pulsing experiments.[42] Together with the measurements of the vacancy formation enthalpy by means of positron annihilation, and with the possibility of measuring small self-diffusivities, ($<10^{-19}\ \mathrm{cm^2\,s^{-1}}$; see Ref. 43), our knowledge of atomic defect properties in intermetallic compounds may be extended down to the low-temperature phases.

We now shall try to discuss the relations between thermal vacancy formation and the structural phase transitions in $Fe_{76.3}Al_{23.7}$ which are observed with increasing temperature. From the vacancy concentrations given in Eq. (4) we conclude that a sufficient number of vacancies are available in order to drive these phase transitions by diffusional processes. For this purpose let us consider the lattice of the DO_3 structure (see Fig. 3), to be built up out of two primitive cubic lattices A and B, each containing either the "central" atoms (Fe I and Al) or the "cube edge" atoms (Fe II), respectively, of a bcc-type structure. Nearest-neighbor jumps can occur only *between* these lattices whereas for vacancy jumps exclusively *within* A or B next-nearest-neighbor distances have to be overcome. For the vacancy jumps in the two directions between A and B, as well as for the non-nearest-neighbor jumps, different jump frequencies ν_i are anticipated. As a consequence, a vacancy may reside predominantly on one type of lattice site. The continuous transition of the DO_3 phase into an increasing fraction of the disordered $A2$ structure, which occurs in the present alloy above 435 °C (see Ref. 7), requires vacancy jumps in both directions for the exchange of Al and Fe atoms between A and B.

At 543 °C the fully ordered DO_3 fraction of the two-phase region is transformed into the partially disordered $B2$ phase. This requires partial exchange of Fe and Al atoms within the A sublattice. It is suggested that this occurs by the activation of a vacancy jump mechanism between next-nearest-neighbor lattice sites on sublattice A.

With increasing temperature, the residual fraction of the $A2$ phase turns into $B2$, a process which is performed by the transfer of the Al atoms to the A lattice and at 600 °C the homogeneous $B2$ phase is attained. The final transition into the $A2$ phase at 645 °C is thought to be enabled by means of highly frequent vacancy jumps between A and B in both directions.

Finally, a few comments should be made as to how far the degree of structural order in a homogeneous phase and the structural or magnetic phase transitions have to be taken into account for an interpretation of the present data.

From x-ray diffraction on quenched Fe–26 at. % Al powders, the equilibrium temperature variations of the degrees of order in the DO_3 and $B2$ phases have been extrapolated,[44] indicating continuous phase transitions of higher order, as reported earlier,[45] with a substantial disordering (~25%) between 200 and 400 °C. Apparently this does not significantly influence the positron lifetime, as concluded from the observation of only a slight linear change of $\bar{\tau}$ (see Fig. 2) as in pure metals. We therefore assume that disordering phenomena in the temperature range of positron trapping do not significantly influence the annihilation characteristics.

The observation that the mean positron lifetime $\bar{\tau}$, and, as deduced from that, the vacancy concentration, increase monotonically with increasing temperature without discontinuities of $\bar{\tau}$ at the phase transitions, which were observed in pure Fe,[26] is not so surprising. It may be due to the fact that, at the phase transitions in the present alloy, a bcc-like structure is maintained, the lattice parameter of which undergoes only minor changes. Only minute changes of the positron annihilation parameters, if any were observed at the order-disorder transitions in Cu_3Au (Refs. 14 and 15) or CuAu (Ref. 14). It should be mentioned that the decomposition mechanisms (spinodal or nucleation and growth) of the transitions $B2\rightarrow A2+B2\rightarrow A2+DO_3$ were investigated in detail by Oki *et al.*[46]

No change of the positron lifetime is observed at the Curie temperature in pure iron.[26] We therefore think that in the present alloy the magnetic order-disorder transition which extends up to the $A2$-$B2$ phase regime (Ref. 47) does not seriously affect the positron annihilation characteristics. It will, however, change the vacancy formation enthalpy by a few hundredths of an electron volt.[26]

In conclusion, we summarize our findings.

(i) The high thermal-equilibrium vacancy concentration in $Fe_{76.3}Al_{23.7}$ is characterized by formation enthalpy $H^F=1.18\pm0.04$ eV.

(ii) From a comparison with the results of self-diffusion studies,[39] the vacancy migration enthalpy $H^M=1.4-1.6$

eV is derived. The influence of thermal vacancy formation on the phase transitions in the present alloy is discussed.

(iii) The degree of structural order and the structural or magnetic phase transition are expected to exert only a minor influence on the positron annihilation characteristics.

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