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Defects in iron aluminides probed with positrons

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ABSTRACT

Positron lifetime spectroscopy and shape analysis of the Doppler broadened positron annihilation peak were performed on iron aluminides containing 28 at.% , 40 at.% and 50 at.% Al. The electronic structure of the open volume defects, probably double vacancies, as seen by positron spectroscopy was independent of the heat treatment. Slight increases of the average positron lifetime as a function of quenching temperature indicate densities of double vacancies sufficiently high to cause the positron wavefunction to overlap with more than one defect. Positron lifetimes corresponding to trapping of vacancy-type defects increased with aluminium content. Changes in the shape of the annihilation peak suggest that the addition of aluminium causes a chemical shift of the iron 3d electrons to lower momenta.

§ 1. INTRODUCTION

The system $Fe_{1-x}Al_x$ is one of the most interesting transition metal aluminide systems with respect to high-temperature application (Rivière and Grilhé 1975, Munroe 1997). Besides the property changes due to different chemical compositions, it is found that vacancies play an important role in the strengthening of FeAl; see for example Chang *et al.* (1993) or Schneibel *et al.* (1996, 1997).

Positron spectroscopy is a very sensitive probe for open volume defects such as vacancies, vacancy clusters or dislocations. In fact, vacancy formation and migration enthalpies have been measured with high precision by means of positron lifetime spectroscopy in a broad variety of metals and alloys, such as Fe_3Al, cf. Schaefer *et al.* (1990) or Wolff *et al.* (1997a). It is known that vacancies in this system occur primarily on the iron sublattice (Paris and Lesbats 1978, Fu *et al.* 1993). Recently, it was shown by internal friction measurements that the thermal vacancies in the stochiometric compound FeAl are most likely double vacancies of second next neighbours on the iron sublattice $[V_{Fe}]_2$ and triple defects, consisting of two iron vacancies and one antisite iron atom $2[V_{Fe}] - Fe_{Al}$ (Damson 1998). The purpose of this work is to explore the influence of the aluminium content on the nature of the thermal vacancies.

§ 2. EXPERIMENTS AND ANALYSIS

The reference samples of 99.999 at.% iron and 99.99 at.% aluminium were polycrystalline material annealed for 1 h in vacuum at 1100°C and 350°C, respectively. The alloy specimens were prepared from (99.99 at.%) iron and aluminium metals, by

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Table 1. Sample specifications and preparations.

Sample	Material	Thermal treatment
FA28-7	$Fe_{72}Al_{28}$	1h @ 1000°C oil quenched
FA40-7	$Fe_{60}Al_{40}$	3d @ 700°C oil quenched
FA50-5	$Fe_{50}Al_{50}$	3d @ 700°C oil quenched 3.7d @ 500°C oil quenched
FA50-6	$Fe_{50}Al_{50}$	3d @ 700°C oil quenched 1d @ 500°C oil quenched
FA50-7	$Fe_{50}Al_{50}$	3d @ 700°C oil quenched
FA50-8	$Fe_{50}Al_{50}$	3d @ 700°C oil quenched 1d @ 800°C oil quenched

arc melting in argon. To establish a thermodynamic equilibrium of vacancies the samples were annealed and quenched as listed in table 1. The thin scale that appeared after oil quenching was removed by electrochemical etching.

The samples were analysed by standard positron lifetime spectroscopy. A fast-fast coincidence positron lifetime spectrometer with Pilot-U scintillators having a resolution function of 220 ps full width of half maximum (FWHM) was used. The source material was 14 μCi ^{22}NaCl solution deposited and dried on a 2 μm thick Al foil, which was placed between two identical specimens (sample–source–sample sandwich). Each spectrum contained 5–7 million single events. Source correction was made as described by Staab *et al.* (1996). The lifetime spectra were numerically analysed using the program LIFESPECFIT (Puska 1978). Repeated measurements confirmed the measured lifetimes.

Doppler broadening measurements were made by recording the energy shifts of both annihilation photons in coincidence. This caused an increased peak–background ratio of $\geq 10^5$ compared with a single-detector set-up (≈ 200), see, for example, Lynn and Goland (1976) or Szpala *et al.* (1996). The spectrometer consisted of two pure germanium detectors facing each other with a distance of 30 cm each to the centre where the sample sandwich was located. The same ^{22}Na source was used for both the lifetime and Doppler broadening measurements. Each 2γ coincidence spectrum contained 2^{24} ($\approx 1.67 \times 10^7$) single events, roughly 96% of which remained after discarding the Compton scattered gamma quanta. For that we added together the events along the lines $E_1 = E_2 + const.$ in a strip of $2m_0c^2 - 1.74\,\text{keV} < E_1 + E_2 < 2m_0c^2 + 1.74\,\text{keV}$, cf. the description in Asoka-Kumar *et al.* (1996). The distribution of Doppler shifts in energy was approximately symmetrical about the channel corresponding to 511 keV. The two sides of the distribution were summed and smoothed, with channel averaging over the FWHM of the spectrometer resolution function.

The S parameter and the W parameter are empirical measures of the degree of broadening. The S parameter is defined as the ratio of the area of the mid portion of the annihilation peak to the area of the entire peak. The W parameter is the ratio of the area of the wings of the peak to its entire area. The width of the regions for both parameters is user-chosen, frequently so that the defect free material has $S = 0.5$ and $W = 0.05$. S parameters are larger when positrons annihilate mostly

with low-momentum electrons. W parameters are larger, and S parameters are smaller, when annihilation occurs with core electrons of atoms, cf. West (1979).

To delineate differences in the summed and averaged spectra, they were normalized to a reference spectrum of pure silicon, Czochralsky-grown and oriented in the [100] direction. We normalized the spectra to the same area, i.e. overall annihilation probability $= 1$, instead of normalization to the same peak annihilation rate as performed by Myler and Simpson (1997), before they were divided channel-by-channel by the reference spectrum. We assume the normalization to the same overall annihilation probability to have the most physical meaning. Prior to the normalization, both reference as well as measured spectrum, were smoothed by adjacent averaging over a number of channels equal to the resolution function of the spectrometer to decrease stochastic noise.

The positron age-momentum correlated spectrum was obtained by using the output of the time–amplitude converter of the positron lifetime spectrometer as second channel in the 2γ coincidence set-up. For that the sample sandwich was placed right in front of the STOP probe facing the germanium detector at 30 cm distance. The START probe was located at an angle of $\approx 120^\circ$ from the STOP probe.

§ 3. Results and discussion

We measured in all samples positron lifetime spectra that consisted of a single component, the value of which increased as a function of the aluminium content, cf. figure 1. The lifetime values give evidence that all positrons are trapped by open volume defects. Our results are in reasonable agreement with those reported by Würschum *et al.* (1995) for thermal vacancies in $Fe_{61}Al_{39}$ ($\tau_1 = 187$ ps), but differ somewhat from those reported by Wolff *et al.* (1997a). They found positron lifetimes of 182 ps and 187 ps for $Fe_{57}Al_{43}$ and $Fe_{52}Al_{48}$, respectively, at 700°C, which are distinctly lower than those measured in this study.

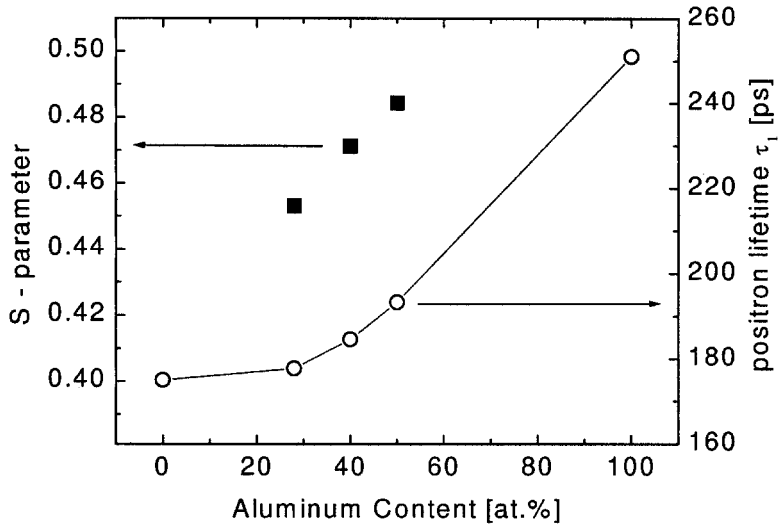

Figure 1. S parameter and defect lifetime τ_1 as a function of aluminium content in samples of $Fe_{1-x}Al_x$ oil-quenched from 700°C; τ_1 values for Fe and Al are from Vehanen *et al.* (1982) and Schaefer *et al.* (1987) respectively; errors are smaller than symbol size, lines are to guide the eye.

Recent experiments with positron spectroscopy, cf. Wolff *et al.* (1997a), and internal friction measurements, cf. Damson (1998), gave good reasons to assume that the thermal defects in stoichiometric $Fe_{50}Al_{50}$ above a temperature of $\approx 700^{\circ}C$ are primarily antisites as well as double vacancies on the iron sublattice, whereas the positron traps in the disordered A2 phase are apparently single vacancies, cf. the positron spectroscopy results of Wolff *et al.* (1997b). Neutron scattering experiments, however, were interpreted as to show vacancies on the Al sublattice, too (Kogachi *et al.* 1998).

Figure 1 shows that the measured lifetime values are close to that for single vacancies in pure iron, $\tau_{1v} = 175$ ps, cf. Vehanen *et al.* (1982). The observed increases in defect lifetime and S parameter with aluminium content agree with the measurements of Wolff *et al.* (1997a) and suggest that the average volume of the trapping sites increases as a function of aluminium content.

The increase in $\overline{\tau}$ and S parameter with the annealing temperature, cf. figure 2, might be interpreted as a change from double vacancies to vacancy aggregates of higher order. Owing to stochastic fluctuations it is possible, on the other hand, that

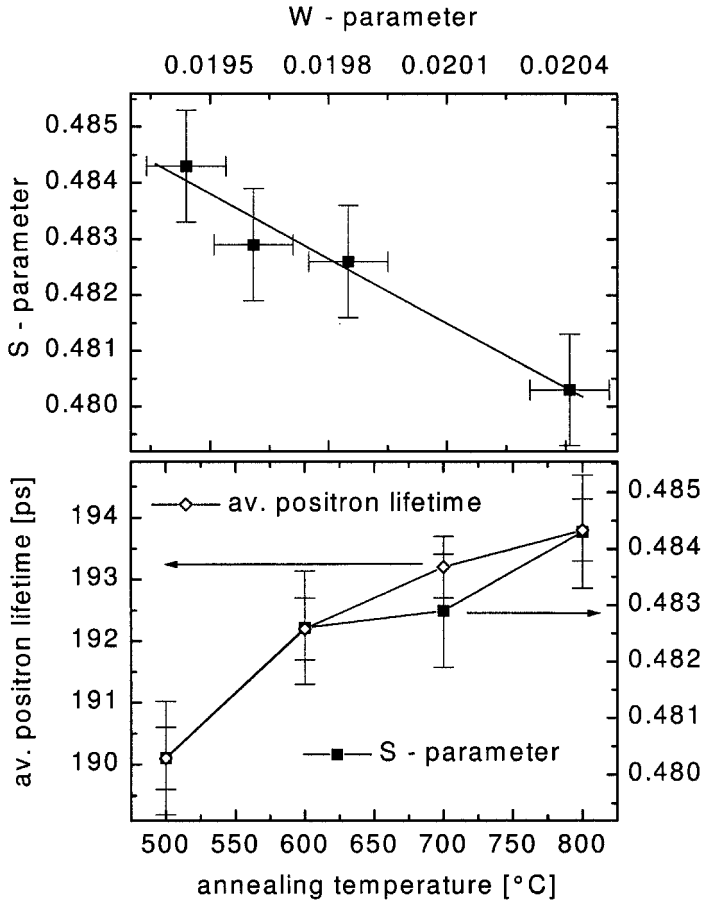

Figure 2. Average positron lifetime and S parameter in stoichiometric FeAl as a function of annealing temperature prior to quenching and S versus W plot; lines are to guide the eye.

after quenching a sufficiently large number of double vacancies, it is close enough for the positron wavefunctions to overlap two of them and, hence, be more confined. We agree with other workers (X. G. Zhang 1998, private communication) that this effect should slightly extend the lifetime of the positrons as well as increase the S parameter. The overall density of open volume defects, on the order of 1 at.% , cf. Chang *et al.* (1993), is high enough to be considered in this case. This is also supported by the S versus W plot in figure 2 which shows a rather straight line, indicating a change in the electronic structure of the trapping sites.

As can be seen from figure 3, the positron annihilation lines obtained from the material containing 40 at.% and 50 at.% Al, respectively, resemble almost completely the line of pure Al. The annihilation line from $Fe_{72}Al_{28}$, however, exhibits roughly the same overall shape as the line from pure iron, although the ratio to the reference is always lower in the entire high energy range $|E_\gamma - m_0c^2| \geq 7.6$ keV. We tried to decompose this peak as a linear combination of the iron and aluminium peaks, but due to the chemical shift, cf. figure 4, this linear combination did not match the line of $Fe_{72}Al_{28}$. The fact that the positron annihilation lines in $Fe_{50}Al_{50}$ and $Fe_{60}Al_{40}$ are only slightly different from that of pure Al seems to indicate that the positrons are trapped at vacancies in the iron sublattice which are surrounded by Al atoms. This would be in agreement with the conclusions of many other authors that vacancies in the system Fe–Al are mainly located on the iron sublattice, e.g. Damson (1998), even if Mössbauer spectroscopy shows that at high temperature iron atoms diffuse partially via vacancies on the aluminium sublattice, cf. Vogl and Sepiol (1994) and Feldwisch *et al.* (1995). On the other hand, it might be possible that, due to electron transfer, the positron is attracted more by the aluminium atoms and, therefore, its wavefunction is biased towards the aluminium sites. To address this question, *ab initio* calculations are proposed. The shape of the quotient spectrum of $Fe_{72}Al_{28}$,

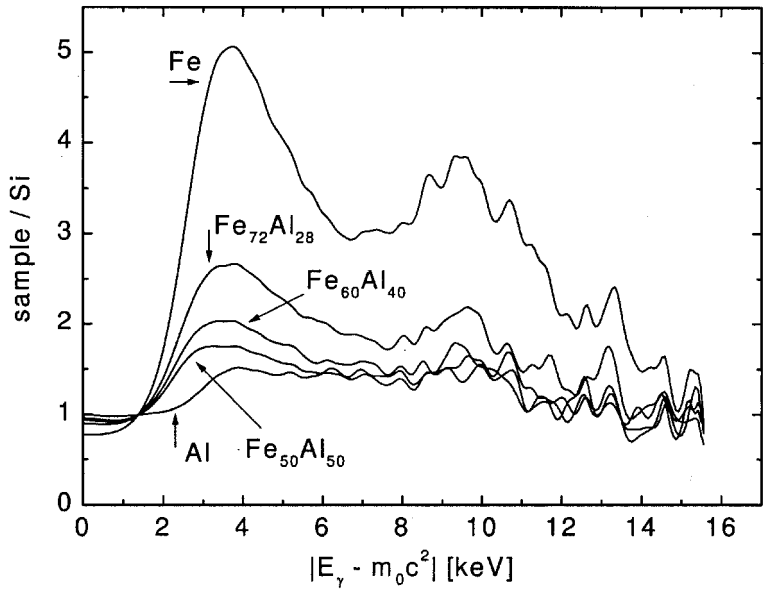

Figure 3. Doppler broadened positron annihilation line in $Fe_{1-x}Al_x$ alloys oil-quenched from 700°C; the lines are normalized to the one of pure silicon.

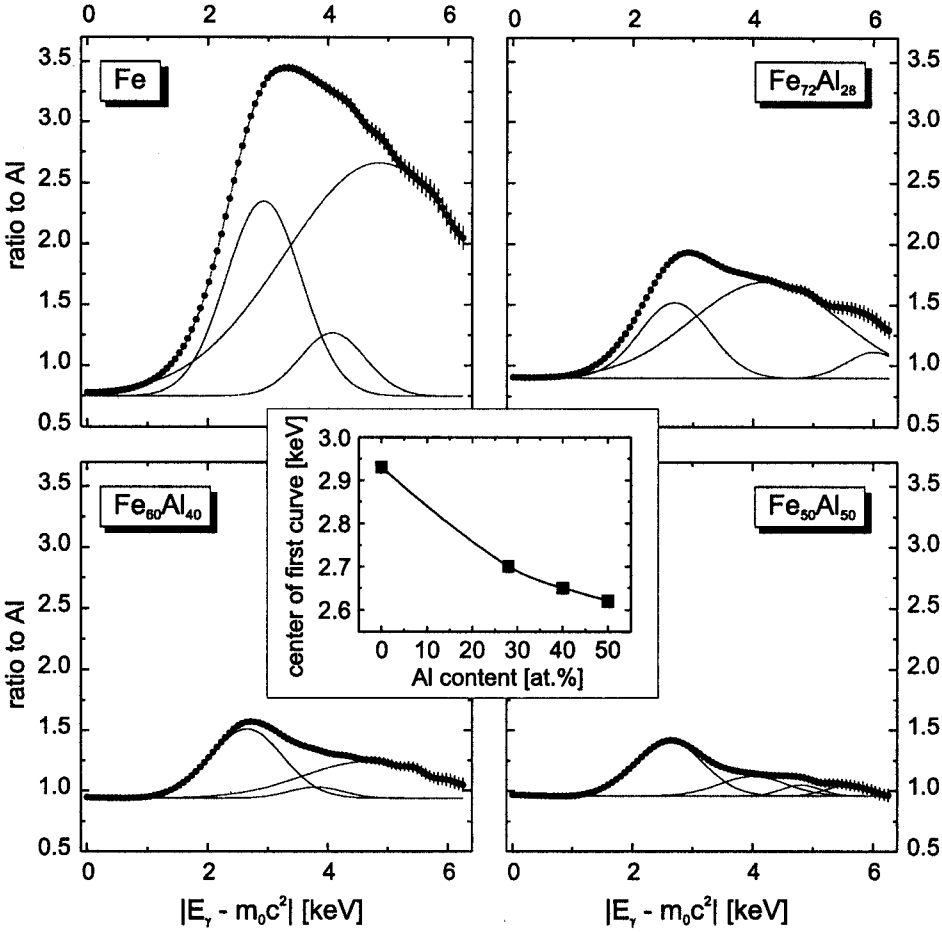

Figure 4. Fit of three Gaussian curves to the positron annihilation line of $Fe_{1-x}Al_x$ normalized to pure Al. The inset shows the centre position of the first fitted curve as a function of the aluminium content; the line is to guide the eye.

however, is similar to that of pure iron, attributed to annihilation with iron electrons. It indicates that the positrons are attracted not only by the aluminium atoms. The environment of the vacancies consists of iron as well as aluminium atoms in the $A2$ structure.

The shape of the normalized positron annihilation peak of pure iron agreed qualitatively with that given by Myler and Simpson (1997). The main peak of our spectrum was located at the same energy $|E_\gamma - m_0c^2| \approx 3.8$ keV as that of Myler and Simpson, but there were distinct differences in the peak shapes for $|E_\gamma - m_0c^2| \geq 8$ keV. It is unknown at present what caused these differences. Different maximum quotients can be attributed to the different normalization, cf. § 2, but not differences in shape.

The shape of the positron annihilation peak for $Fe_{50}Al_{50}$ was independent of the annealing temperature, consistent with the positron lifetime results. The quotient spectra derived from the peaks measured after the different quenches would all fit a curve slightly broader than that shown in figure 3 for the 700°C specimen. These

results indicate that the chemical environment of the trapping sites remained basically the same after the different heat treatments. Distinct differences, however, were found in the very sensitive S parameters and W parameters, as shown in figure 2, which is attributed to different defect densities only.

The normalized spectra in figure 3 indicate that the addition of aluminium causes the main peak, corresponding to iron, to be shifted to different energies. To better illustrate this, the data in figure 4 are normalized to pure aluminium rather than to pure silicon as in figure 3 to bring out the differences in the electronic structure. We concentrate on the energy range $|E_\gamma - m_0c^2| \leq 6.25$ keV. Clearly, the maximum of the peak shifts to lower energies as the aluminium content increases. By an empirical approach similar to that of Myler and Simpson (1997), we fitted three Gaussian curves to the quotient spectra. The inset in figure 4 shows that the centroid of the main Gaussian (lowest energy) shifts from a difference of 2.93 keV with respect to m_0c^2, to a difference of 2.63 keV. Assuming the effective mass to be similar to the rest mass, $m_{\text{eff}}/m_0 \approx 1$, the energy shift of the γ quanta would arise from a shift in the kinetic energy of the involved electrons from 33.6 eV to 27 eV. We tentatively interpret this effect as due to the incorporation of the iron 3d electrons into the band states of the alloy. The delocalization, perhaps, caused the momenta of the iron electrons to be lowered.

It is questionable whether or not the high density of defects will significantly alter or even destroy the band structure of the intermetallic alloys. This gives rise to the possibility that prethermal or pretrapping annihilation causes the observed changes in the electron momenta. To exclude this possibility we measured an age-momentum correlated spectrum (AMOC), cf. the article of Siegle *et al.* (1997) for the $Fe_{50}Al_{50}$ sample, which had the highest density of defects. As can be seen from figure 5, the S

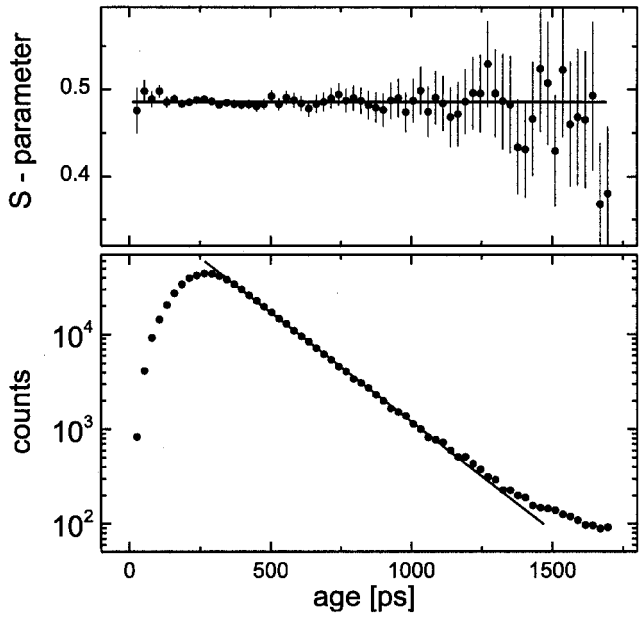

Figure 5. S parameter as a function of positron age in $Fe_{50}Al_{50}$ (sample FA50-7, cf. table 1) and corresponding positron lifetime spectrum. Slight deviations from the straight line are due to contributions from the positron source.

parameter, and, therefore most likely, the entire electron environment is independent of the age of the positron. Hence, the observed shift of the annihilation gamma quanta is really due to lowered electron momenta. Owing to the low count rate of $\approx 2.6\,s^{-1}$ we were limited to $\approx 6 \times 10^5$ counts per spectrum, which prevented more detailed studies of the annihilation line as a function of the positron age.

§ 4. Conclusions

Positron lifetime and the Doppler broadened positron annihilation line were measured in oil quenched iron aluminium samples of different stoichiometry. In all samples the density of the quenched-in defects was sufficient to trap all positrons. We found single lifetimes only, indicating one major kind of defect. The lifetime values found were consistent with conclusions in the literature that at aluminium contents of 40 at.% and greater the defects are predominantly double vacancies.

Slight increases in lifetime and S parameter as a function of quenching temperature are interpreted as due to the very high density of double vacancies, causing the positron wavefunctions to overlap more than one site.

The annihilation peak arising from positrons trapped at double vacancies in $Fe_{60}Al_{40}$ and $Fe_{50}Al_{50}$ resembles the peak of pure aluminium, supporting the theory that thermal vacancies in those alloys are mainly located in the iron sublattice.

By means of 2γ coincidence Doppler broadening spectroscopy it was found that the momenta of some of the iron electrons, probably the 3d, with which the positrons annihilate decrease with an increasing amount of aluminium in the alloy.

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