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Structural and thermal defects in Pd–In alloys

W Puff†, T Friessnegg†, A G Balogh‡ and H Wever§

† Institut für Kernphysik, Technische Universität Graz, A-8010 Graz, Austria
‡ Fachbereich Materialwissenschaft, Technische Hochschule Darmstadt, Darmstadt, Germany
§ Institut für Metallforschung, Technische Universität Berlin, Berlin, Germany

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Abstract. We report the results of positron lifetime and Doppler-broadening measurements in Pd–In β Hume-Rothery alloys. The combination of these techniques gave new insights into the defect structure of annealed and quenched samples of different compositions. The existence of thermal In vacancies for some compositions has been confirmed.

1. Introduction

Ordered β Hume-Rothery alloys (AB) with the CsCl (B2) structure, such as Fe–Al, Co–Al, Co–Ga, Ni–Al, Ni–Ga and Pd–In, are known to exist over a relatively wide range of compositions. In such metallic compounds, one component (A) has a filled or nearly filled d shell and the other component (B) has two or three valence electrons. All compounds have a rather broad homogeneity range (e.g. 48–61 at.% Pd for Pd–In). In order to retain their ordered B2 structure, even for strong deviations from stoichiometry, structural (temperature-independent) defects are formed in the respective systems. For A-rich compounds, these defects are antistructure (or antisite) atoms in the B sublattice while, in the B-rich compounds, A vacancies are created. This model proposed by Bradley and Taylor (1937) was confirmed with small corrections for different alloys by several other groups (Fort *et al* 1973, Müller and Hahn 1984, Hahn *et al* 1985, Hünecke 1985, Hünecke *et al* 1987). In addition to these constitutional defects, thermal defects in high concentrations (about 1–2 at.%, typically) were observed in these phases at elevated temperatures. The mechanism of the defect creation is not fully understood, and suggested models (Wasilewski 1968) could not be confirmed in all details. Especially interesting is the change in the defect structure in the temperature range 700–750 °C found in Pd–In by Simmons–Balluffi-type measurements (Hünecke 1985, Hünecke *et al* 1987). In the low-temperature range, the triple defect ($2V_{Pd} + Pd_{In} \leftrightarrow V_{In} + V_{Pd}$) has been suggested to be responsible and, in the high-temperature range, double vacancies (V_{Pd}, V_{In}). In this work we used high-resolution positron lifetime and Doppler-broadening measurements to find and identify the different types of vacancy and the more complex defect clusters in both slowly cooled (structure defects) and quenched (structural as well as thermal defects) samples over the whole ordered composition range ($Pd_{48}In_{52}$, $Pd_{49}In_{51}$, $Pd_{50}In_{50}$, $Pd_{51}In_{49}$ and $Pd_{56}In_{44}$).

2. Experiment

Samples were prepared from high-purity Pd and In by high-frequency inductive heating in a graphite crucible under an extra-pure Ar atmosphere. After homogenization, discs of

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10 mm diameter and about 0.5 mm thickness were cut with a diamond saw and polished mechanically. The methods used to characterize the samples have been described by Hünecke (1985). Moreover, the concentrations of the two composites were determined by energy-dispersive x-ray spectroscopy. For slow cooling experiments, specimens were heated to 1000 °C and then cooled to room temperature at a rate of 10 K h^{-1} and between 800 and 500 °C at 5 K h^{-1}. For quenching, specimens were heated to the desired temperature (650 or 850 °C) for 30 min and were then allowed to fall directly into a water bath. For the positron measurements, up to three sets of samples for each composition were used.

The positron annihilation lifetime and Doppler-broadening measurements were performed at room temperature. For the lifetime measurements, a conventional lifetime spectrometer was used with a time resolution of 220 ps full width at half-maximum (FWHM). The positron source itself was used in the well known sandwich configuration and was prepared by deposition of about 10 μCi of ^{22}NaCl on a 0.81 mg cm^{-2} Al foil. Each lifetime spectrum was accumulated over a 24 h period which gave about 1×10^7 counts. After source correction, the spectra were analysed by the PFPOSFIT program (Puff 1983). This program fits a number of lifetime components and their respective intensities together with the resolution function of the measuring system to the measured spectrum. The value of an individual lifetime component is determined by the positron state at the site of the annihilation (i.e. bulk or defect states), while the corresponding intensities are related to the number of positrons annihilating from this state.

In this investigation, all the lifetime spectra could be decomposed into three or four components. The longest was, however, an essentially constant term of about 1.5 ns with not more than 0.3% intensity. This term could easily be separated from the actual spectra and will not be discussed further. In the statistical analyses of the spectra the 'variance of the fit' is calculated. This quantity, which is approximately a normal distribution, serves as an indication of the validity of the model used. Values substantially greater than 1 suggest that the model is not a good representation of the measured spectrum. In this case the number of lifetime components can be increased. If the analysis with the new model function gives a better variance of the fit, the new model is from a statistical point of view a better description of the annihilation spectrum.

The Doppler broadening of the annihilation line was measured using an intrinsic Ge detector with a resolution (FWHM) of 1.18 keV at 497 keV. Each measurement lasted 1000 s and was repeated at least ten times. A total of about 2×10^6 counts was recorded for each spectrum. The usual S parameter (the ratio of the counts in a central portion of the spectrum to the total counts) was used to characterize the spectra.

3. Results and discussion

3.1. Structural defects

In figure 1 the mean lifetime τ and the S parameter for the annealed samples as functions of the Pd concentration are shown. The results are in good agreement with earlier results on similar samples (Balogh *et al* 1985, Puff *et al* 1992). The composition with 48 at.% Pd shows the highest values for both the mean lifetime and S. Both parameters have their minimum values for the stoichiometric sample, an indication that the concentration of structural defects in this sample is the smallest. For the Pd-rich compositions the values of the mean lifetime and S again show an increase. The different values of the parameters as functions of the Pd content show that the defects on both sides of the stoichiometric composition are not the same. This finding is in agreement with the results of Hünecke

(1985) obtained from the difference between the x-ray and pycnometric density. According to these measurements the main defects are, in the In-rich alloys, vacancies in the palladium lattice (V_{Pd}) and, in the Pd-rich compounds, Pd antisite atoms in the In sublattice (Pd_{In}). According to that model, two additional Pd atoms in the Pd-rich compound result in the formation of an antisite atom, whereas in the In-rich alloys for each overstoichiometric In atom a vacancy will be formed. Therefore, the number of defects formed on the Pd-rich side is half the number on the In-rich side for equal distance from stoichiometry.

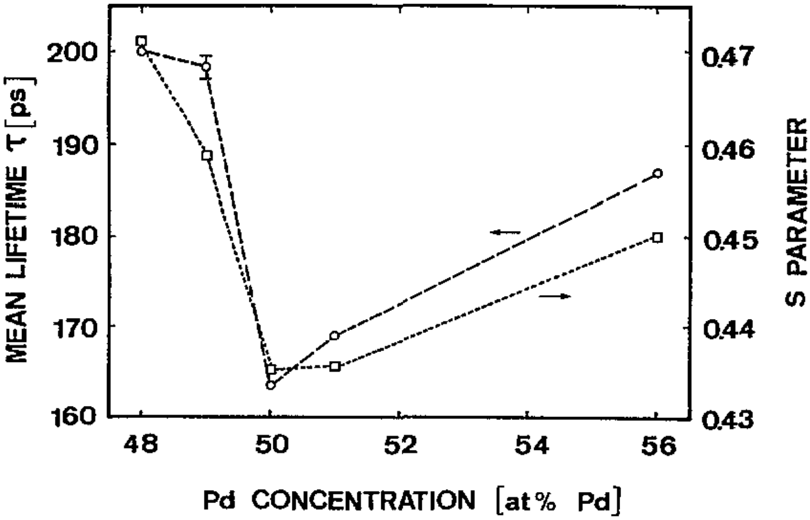

Figure 1. Mean lifetime (○) and Doppler parameter S (□) as functions of the Pd concentration.

Figure 1 shows for the Pd-rich phases a weaker increase in the mean lifetime as well as in S in comparison with the alloys with a higher concentration of In atoms. Hünecke (1985) showed that the concentration of structural vacancies decreases continuously with increasing Pd content.

Table 1 shows the lifetime values and the corresponding intensities after a two-term analysis together with the defect concentrations as obtained by Hünecke (1985). The increase in the intensity of the longer lifetime (defect) component on the In-rich side is larger compared with the Pd-rich side (e.g. 76% for $Pd_{49}In_{51}$ and 56% for $Pd_{51}In_{49}$). It is surprising that the defect intensity in the In-rich samples does not exceed 77% although the defect concentration is very high (up to about 4 at.%). The reason for this might be a substantially smaller value for the positron trapping rate of about 10^{12} s^{-1} in these compounds (Puff *et al* 1992), compared with 10^{14}–10^{15} s^{-1} for pure metals. There is no further increase in the intensity I_2 of the defect component from the $Pd_{49}In_{51}$ sample to $Pd_{48}In_{52}$ even though there is a doubling in the vacancy concentration. We relate the lifetime of 226 ps in the $Pd_{48}In_{52}$ sample to Pd vacancies (V_{Pd}), since these are the main defects for this composition.

Table 1 shows that with increasing Pd content the concentration of structural vacancies decreases. Unfortunately, one cannot decide from the Simmons–Balluffi experiments (Hünecke 1985) in which sublattice the vacancies are present. However, our results show an increase in the intensity of the defect component also for the Pd-rich samples relative to the stoichiometric sample. The defect lifetime, on the other hand, becomes shorter. Obviously,

Table 1. Lifetimes, intensities and the concentration of structural defects. C_V and C_A are the fractions of vacancies and antisite atoms, respectively, as obtained by Hünecke (1985).

Sample (at.% Pd)	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	C_V (at.%)	C_A (at.%)
48	111	23	226	77	4	
49	114	24	225	76	2	
50	101	48	221	52	0.1	<0.05
51	105	44	219	56	0.07	1
56	117	29	216	71	<0.05	6

the defect mechanism in the Pd-rich samples is more complicated than in the In-rich samples. There should be In vacancies formed in this phases. Although the concentration of these vacancies might be very small, since they are not observed in other experiments, they could give a contribution to the observed defect lifetime component. Table 1 also shows an increase in the concentration of the Pd antisite atoms (Pd_{In}) with increasing Pd content. It could easily be the case that the Pd antisite atoms represent attractive defects for the positrons. The positron lifetime in these defects should be shorter than in the Pd vacancies, because of the higher electron density. If one compares the increase in S and the mean lifetime for the Pd-rich samples, one finds a weaker increase in S. This finding suggests that, in this composition range, the defects have a stronger influence on the electron density than on the momentum distribution of the electrons.

3.2. Thermal defects

After thermal treatment (quench from 650 or 850 °C), different behaviours for the various samples are observable (figures 2 and 3). The mean lifetime and the S parameter for the $Pd_{50}In_{50}$ and $Pd_{51}In_{49}$ samples increase markedly. For the other compositions the mean lifetime is more or less constant, whereas S decreases after quenching.

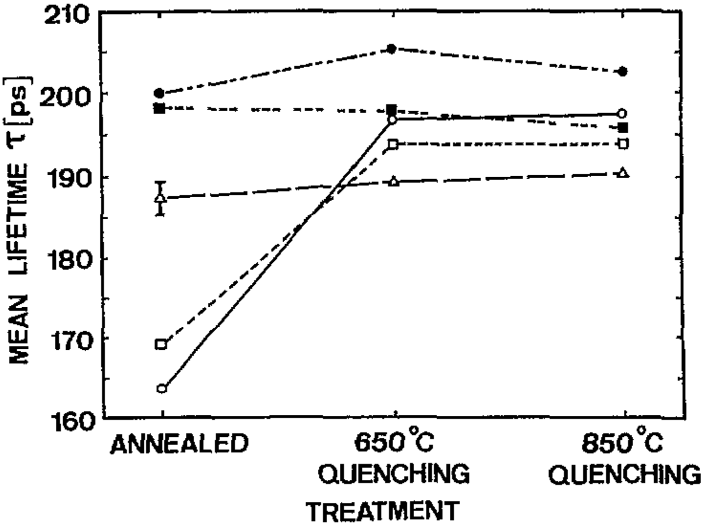

Figure 2. Mean lifetime for the various samples as a function of sample treatment: ●, $Pd_{48}In_{52}$; ■, $Pd_{49}In_{51}$; ○, $Pd_{50}In_{50}$; □, $Pd_{51}In_{49}$; △, $Pd_{56}In_{44}$.

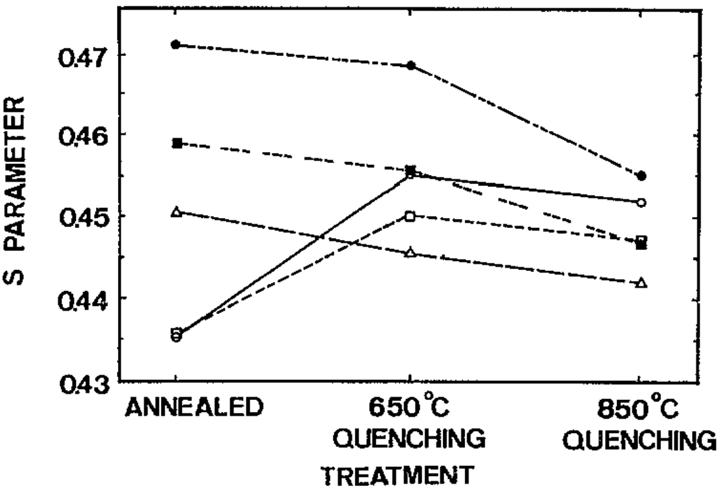

Figure 3. Doppler parameter S for the various samples as a function of sample treatment: ●, $Pd_{48}In_{52}$; ■, $Pd_{49}In_{51}$; ○, $Pd_{50}In_{50}$; □, $Pd_{51}In_{49}$; △, $Pd_{56}In_{44}$.

The marked increases in τ and S for $Pd_{50}In_{50}$ and $Pd_{51}In_{49}$ indicate the appearance of thermal vacancies in these samples after quenching from 650 °C. The increase is largest for the stoichiometric sample. Obviously, defects can be built into the sample most easily in the case of a symmetric distribution of the two composites. The very small increase in τ for $Pd_{56}In_{44}$ confirms this concept.

For $Pd_{49}In_{51}$ and $Pd_{48}In_{52}$, we could not find any increase in the positron parameters after thermal quenching from 650 °C. The reason is the already very high concentration of structural vacancies. Hünecke (1985) showed that the concentration of defects for the composition $Pd_{49}In_{51}$ is nearly constant up to 750 °C. One can expect a similar behaviour for $Pd_{48}In_{52}$, since in this sample the concentration of structural defects is even higher.

Figure 4 shows the mean lifetime τ and S as functions of the Pd concentration after quenching the samples from 650 °C. We see a continuous decrease in both parameters with increasing Pd concentration.

In table 2 the results of a two-term analysis of the lifetime spectra is shown. For the stoichiometric $Pd_{50}In_{50}$ sample the intensity I_2, of the defect component increases from 52% for the annealed sample to 80%. For the $Pd_{51}In_{49}$ sample the increase amounts to 10%, from 56% to 66%. For the $Pd_{50}In_{50}$ sample the analysis yields a larger intensity of the longer-lifetime component than for the $Pd_{49}In_{51}$ sample, even though the defect concentration in the latter is higher by a factor of ten (Hünecke 1985). The reason for that could be the existence of another defect in the stoichiometric $Pd_{50}In_{50}$ sample besides the thermal vacancies in the Pd sublattice (V_{Pd}). This defect would have to be very attractive for the positrons to explain the over-proportional increase in the mean lifetime and the S parameter. Pd antisite atoms can be excluded because of the high electron density in comparison with vacancies. As a consequence, the triple-defect mechanism is very unlikely for this composition. Possible candidates then are thermal In vacancies. Moreover, in the immediate vicinity to vacancies in the Pd sublattice (V_{Pd}), pairs of vacancies are formed, which are even more attractive to the positrons.

In a next step, we tried to split the longer-lifetime component into two components to resolve the different defects. For $Pd_{50}In_{50}$, $Pd_{51}In_{49}$ and $Pd_{56}In_{44}$ we were successful in

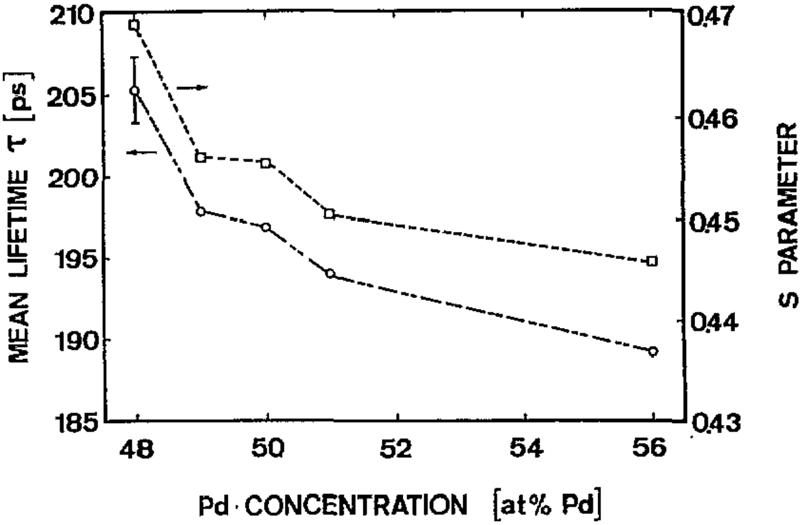

Figure 4. Dependences of the mean lifetime τ (○) and the Doppler parameter S (□) on the Pd concentration after quenching the samples from 650 °C.

Table 2. Results of a two-term analysis of the spectra after quenching from 650 °C.

Pd (at.%)	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)
48	112	21	230	79
49	131	31	228	69
50	110	20	219	80
51	134	34	225	66
56	136	41	227	59

Table 3. Results of the three-term analysis of the samples quenched from 650 °C. τ_{Di} and I_{Di} are the defect lifetimes and the corresponding intensities. I_{tot} is the total intensity.

Pd (at.%)	τ_{D1} (ps)	I_{D1} (%)	τ_{D2} (ps)	I_{D2} (%)	I_{tot} (%)
50	199	74	289	14	88
51	197	71	283	14	85
56	197	73	304	9	82

performing a three-term analysis of the lifetime spectra. Table 3 shows the lifetimes and the corresponding intensities for the two defect components.

According to the discussion above, we relate the two defect lifetimes $\tau_{D1} \simeq 200$ ps and $\tau_{D2} \simeq 280$–290 ps to In vacancies and vacancy pairs, respectively. Moreover, one should have in mind that in these samples also thermal Pd vacancies (V_{Pd}) are formed during heating. Since the positron lifetime in these vacancies amounts to 226 ps, very close to the shorter defect lifetime, a clear distinction of these defects was not possible in our experiments. In fact, the contribution of these defects is included in the intensity I_{D1}. The vacancy lifetime in pure In is about 272 ps (Puff *et al* 1983). For pure Pd, the vacancy lifetime should be about 170–180 ps. This value follows from the bulk lifetime 108–118 ps

(Alekseeva *et al* 1979, Suzuki *et al* 1979) under the assumption that the vacancy lifetime is a factor of 1.4–1.5 longer than the bulk value, which is fulfilled for most metals (MacKenzie 1983). However, in an ordered Pd–In alloy it has to be inverse, because a Pd vacancy is always surrounded by In atoms and therefore corresponds to an In vacancy in the pure metal, and on the other side the next neighbours of an In vacancy are Pd atoms. Of course, the crystal structures and the numbers of nearest neighbours are different. Moreover the influence of the lattice relaxation is not known in the compounds. As a consequence, the lifetime values in the vacancies do not correspond to the values in the pure metals.

After quenching the samples from 850 °C there is no change in the mean lifetime. The only change is in S for $Pd_{48}In_{52}$ and $Pd_{49}In_{51}$ (see figure 3). This suggests a change in the defect structure in these samples which is not seen in the other compositions. The interpretation of this effect is not easy since the thermal defect mechanism for the In-rich alloys is not observable in our experiments. Because of the high concentration of structural defects the positrons are not sensitive to a further increase in the number of defects. If a triple defect (Wasilewski 1968) is formed in the samples, there should be Pd antisite atoms (Pd_{In}) in the $Pd_{48}In_{52}$ and $Pd_{49}In_{51}$ samples after quenching from 650 °C. With increasing temperature these antisite atoms become mobile. A possible explanation could be that, during quenching, the antisite atoms take an interstitial position, leaving behind a vacancy. In this model, a Pd antisite atom forms a vacancy and an interstitial Pd atom ($1Pd_{In} \rightarrow 1V_{In} + 1Pd_i$). This defect has different effects on the mean lifetime and on S. A similar effect has already been observed in semiconductors (Puff *et al* 1989).

There could be another interpretation for the different behaviours of the mean lifetime and S after quenching from 850 °C for $Pd_{48}In_{52}$ and $Pd_{49}In_{51}$. As Hünecke (1985) showed, the number of thermal vacancies for $Pd_{49}In_{51}$ during heating to 700 °C is constant and increases only at higher temperatures. The increase is much smaller than for the stoichiometric $Pd_{50}In_{50}$ sample. At about 850 °C, the increase in the vacancy concentration for $Pd_{49}In_{51}$ is only about 0.05 at.% compared with the concentration of structural defects. If one assumes again the validity of the triple-defect mechanism, one has in addition to the thermal Pd vacancies (V_{Pd}) also 0.025 at.% Pd antisite atoms (Pd_{In}). It is conceivable that these defects have different effects on S and the mean lifetime.

Table 4 shows the results of a three-term analysis of the samples after quenching from 850 °C. It is worth noting that we were also successful for $Pd_{48}In_{52}$ in analysing the spectra with three lifetime components.

Table 4. Results of the three-term analysis of the samples quenched from 850 °C.

Pd (at.%)	τ_{D1} (ps)	I_{D1} (%)	τ_{D2} (ps)	I_{D2} (%)	I_{tot} (%)
48	189	71	290	20	91
50	196	72	289	15	87
51	198	74	304	10	84
56	190	75	304	12	87

After quenching from 850 °C, no further increase in the defect concentration for $Pd_{50}In_{50}$ and $Pd_{51}In_{49}$ compared with the 650 °C quenching can be seen (table 3). Obviously, the number of defects is already so high that the positrons are not sensitive to a further increase in this concentration any more.

The observation of thermal In vacancies in $Pd_{48}In_{52}$ is a strong indication for the formation of interstitial Pd atoms (Pd_i) in this phase, as discussed above.

For $Pd_{49}In_{51}$ it was not possible to split the defect lifetime component into two different parts. Obviously, in this sample the probability of forming vacancy pairs (V_{Pd}, V_{In}) is too small to be observable in our experiments. The immediate vicinity of an interstitial Pd atom (Pd_i), on the other hand, could influence the momentum distribution of the electrons and therefore explain the smoother decrease in S in this sample in comparison with $Pd_{48}In_{52}$.

For the compound with 56 at.% Pd there are enough Pd antisite atoms as structural defects in the sample; therefore the defect mechanism $1\ Pd_{In} \rightarrow 1\ V_{In} + 1\ Pd_i$ could explain the different behaviours of the mean lifetime and S after quenching from 850 °C.

3.3. *Low-temperature measurements*

After each thermal treatment we also measured the lifetime and S as functions of temperature from room temperature down to 10 K. This investigation was triggered by results from Kim *et al* (1993) on Ag–Mg, which showed that single, negatively charged vacancies are necessary to keep the concentration of valence electrons constant and thus inhibit a rise in the Fermi energy. In a positron experiment, charged defects can be identified by the trapping cross section, which has a rather strong temperature dependence for charged vacancies (Dannefaer 1990). The trapping cross section is given by the trapping model (Hautojärvi 1979).

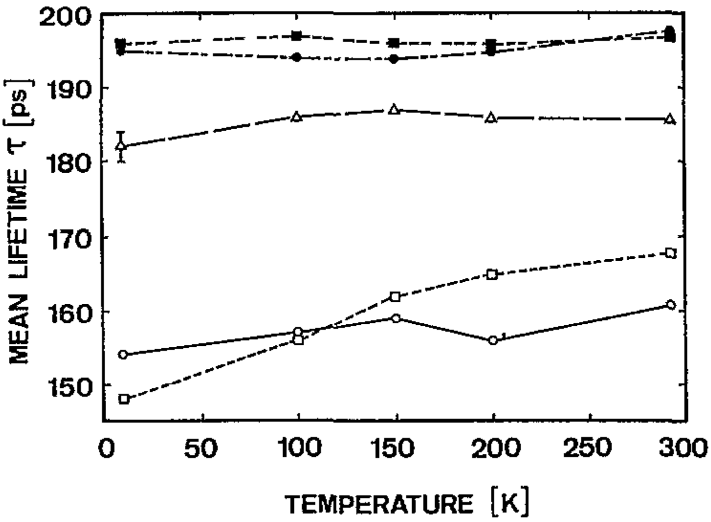

Figure 5. Mean lifetime for the annealed samples as a function of the measuring temperature: ●, $Pd_{48}In_{52}$; ■, $Pd_{49}In_{51}$; ○, $Pd_{50}In_{50}$; □, $Pd_{51}In_{49}$; △, $Pd_{56}In_{44}$.

In figure 5, the mean lifetime for the annealed samples is shown as a function of the measuring temperature. There is no temperature dependence for the In-rich samples and only a weak variation for $Pd_{50}In_{50}$ and $Pd_{51}In_{49}$ after annealing and quenching from 650 °C (figure 6). After quenching from 850 °C there is no temperature dependence at all (Friessnegg 1994).

In table 5 the results of a three-term analysis of $Pd_{50}In_{50}$ after quenching from 650 °C, together with the value of the mean lifetime and S, are shown. The longer defect lifetime τ_{D2} associated with the vacancy pairs was fixed at 289 ps. For $Pd_{51}In_{49}$ the results are very similar.

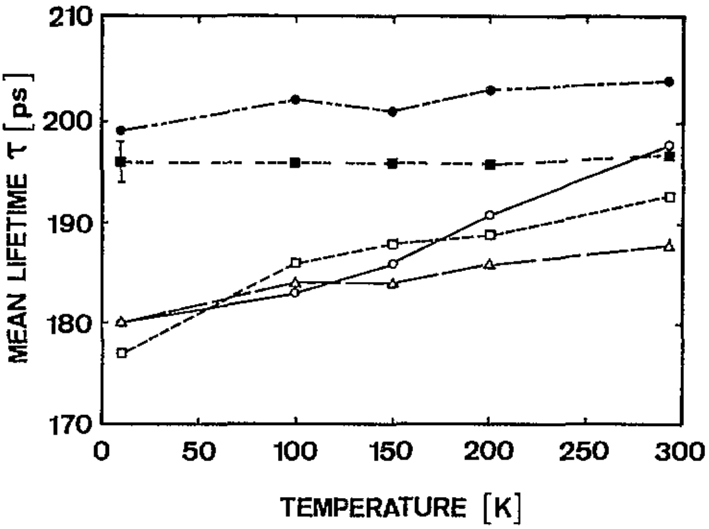

Figure 6. Mean lifetime as a function of temperature for the samples quenched from 650 °C: ●, $Pd_{48}In_{52}$; ■, $Pd_{49}In_{51}$; ○, $Pd_{50}In_{50}$; □, $Pd_{51}In_{49}$; △, $Pd_{56}In_{44}$.

The intensity I_{D1} varies with temperature. This lifetime component has been related to thermal In vacancies. Since the concentration of the frozen-in In vacancies should not change with decreasing temperature it seems that the positrons are trapped at least partly in other defects, from where they can escape at higher temperatures.

Table 5. Lifetimes of the defect components and corresponding intensities, mean lifetime and Doppler parameter S for $Pd_{50}In_{50}$ after quenching from 650 °C as functions of the measuring temperature.

Temperature (K)	τ_{D1} (ps)	I_{D1} (%)	τ_{D2} (ps)	I_{D2} (%)	τ (ps)	S
10	193	63	289	12	180	0.4437
100	195	63	289	13	183	0.4454
150	213	69	289	5	186	0.4481
200	212	72	289	7	191	0.4515
293	199	74	289	14	198	0.4554

Summing up, it may be said that from the low-temperature measurement we cannot deduce the existence of charged vacancies for our Pd–In samples.

4. Conclusions

It was for the first time possible to separate three different lifetimes in intermetallic compounds. The main results may be summarized as follows.

(i) It has been shown that positrons can be trapped by constitutional Pd vacancies. The positron lifetime in this defect is 226 ps.

(ii) There is evidence for the existence of thermal In vacancies with a positron lifetime of 200 ps.

(iii) The longer defect component with a lifetime of about 280–290 ps is related to vacancy pairs.

(iv) From the low-temperature measurements, for our Pd–In samples, we cannot deduce the existence of charged vacancies.

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References

Alekseeva O K, Onishchuk V A, Shantarovich V P, Dekhtyar I Ya and Shevchenko V I 1979 *Phys. Status Solidi* b **95** K135
Balogh A G, Dezsi I, Hahn H and Ghafari M 1985 *J. Phys. F: Met. Phys.* **15** 1623
Bradley A J and Taylor A 1937 *Proc. R. Soc.* A **159** 56
Dannefaer S 1990 *Defect Control in Semiconductors* ed K Sumino (Amsterdam: North-Holland) p 1561
Fort D, Smallman R E and Harris I R 1973 *J. Less-common Met.* **31** 263
Friessnegg T 1994 *Diplomarbeit* (Graz: Technical University)
Hahn H, Ghafari M, Dieudonne R and Gonser U 1985 *Scr. Metall.* **19** 615
Hautojärvi P 1979 *Positrons in Solids* (Berlin: Springer)
Hünecke J 1985 *Thesis* (Berlin: Technical University)
Hünecke J, Kim I, Frohberg G and Wever H 1987 *Mater. Sci. Forum* **15–18** 1311
Kim I, Frohberg G and Wever H 1993 *Z. Metallk.* **84** 237
MacKenzie I 1983 *Positron Solid-State Physics* ed W Brandt and A Dupasquier (Amsterdam: North-Holland) p 196
Müller H G and Hahn H 1984 *Phil. Mag.* A **50** 71
Puff W 1983 *Comput. Phys. Commun.* **13** 371
Puff W, Balogh A G and Wever H 1992 *Mater. Sci. Forum* **105–10** 1181
Puff W, Mascher P, Kerr D and Dannefaer S 1989 *Mater. Sci. Forum* **38–41** 225
Puff W, Mascher P, Kindl P and Sormann H 1983 *Phys. Status Solidi* b **118** 799
Suzuki K, Itoh H, Hasegawa M, Fukunaga T and Honda T 1979 *Positron Annihilation* ed R R Hasiguti and K Fujiwara (Sendai: The Japan Institute of Metals) p 861
Wasilewski R J 1968 *J. Phys. Chem. Solids* **29** 39