7. On the temperature dependence of positron trapping in GaAs

The practical importance of positron annihilation as a method for semiconductor studies lies in its unique ability to measure the absolute concentrations of vacancy-like defects and depends extremely on the accuracy of these measurements. The latter is constrained by the knowledge of the trapping coefficient μ, which represents a constant of proportionality between the measured trapping rate K and concentration C_d of a certain defect-type. (Eq. 3.4). In order to determine the trapping coefficient, the vacancy concentration must be measured independently of the positron experiment by using a reference method (Krause-Rehberg and Leipner 1997). Unfortunately, the information provided by such methods is always indirect. Therefore, μ is *at best* known with an accuracy factor of two. Moreover, the trapping coefficient is usually obtained at room temperature, whereas positron annihilation is often most sensitive and hence its results are most reliable at low temperatures. These uncertainties invalidate the significance of positron annihilation as a quantitative method, despite the high precision of measurements (about 1% for positron annihilation lifetime spectroscopy).

In this respect, the information obtained from temperature-dependent measurements can have more deterministic and quantitative character than the determined absolute vacancy concentrations, since these results represent just the change of annihilation parameters (τ_{av} or K) with temperature, whereas no normalization on positron trapping coefficient is necessary. However, despite the fact that positron annihilation has been applied to study of semiconducting materials for more than 30 years, the influence of the temperature on the positron trapping rate in semiconducting materials is still not well understood. Theoretical works performed in the late 80's (Section 3.2.1) provided description of the positron trapping temperature dependence in good (at least qualitative) agreement with experimental results available at those times. This enabled developing of simple trapping models for fitting to the experimental data (Section 3.2.2). Satisfied with this success, both theoretical and experimental investigations of the essence of the positron trapping coefficient temperature dependence were stopped. Experimentalists dealing with positron annihilation temperature-dependent measurements interpret their results either in the frameworks of the positron trapping models mentioned above or resort to purely qualitative arguments, such as temperature-driven defect charge transition (Gebauer et al. 2001) or resonance trapping (Shirai and Takamura 1989), if these models turn out to be not applicable. The present author strongly believes that the valuable information about positron-defects interaction contained in the temperature behavior of positron trapping remains unused due to a lack of understanding.

It is the goal of this chapter to demonstrate the importance of temperature influence on positron annihilation parameters and to show the necessity of its further theoretical and experimental investigations. Two expedients are used to achieve the task. Firstly, inconsistency of the existing model of temperature-dependent positron trapping with some experimental results is shown (Section 7.1). No theoretical development of a new trapping model was intended here. This subject deserves an individual investigation. Secondly, all the positron annihilation lifetime results obtained in this work were systematized according to the temperature dependence of the trapping rate, i.e. average positron lifetime. It is the authors hope that such analysis will contribute to a better understanding of the temperature dependence of positron trapping in semiconductors. In particular, the following questions were discussed:

1) How does the temperature dependence of the trapping rate K(T) depend on the concentration of vacancy-like defects?
2) What is the influence of the defect charge state on K(T)?
3) Does K(T) depend on the vacancy charge state?
4) Below which temperatures are positrons effectively trapped by shallow traps?
5) How does the shallow trap concentration influence these temperatures?

7.1 GaAs:Si vs GaAs:Te

The defect structure of silicon- and tellurium-doped GaAs are very similar. Both these materials are self-compensated n-type semiconductors, in which Si_{Ga} or Te_{As} donors are partly deactivated due to formation of acceptor-like donor-gallium vacancy complexes, $Si_{Ga}V_{Ga}$ and $Te_{As}V_{Ga}$, and, in case of GaAs:Si, additionally by silicon acceptors, Si_{As}[1]. The formation of donor-V_{Ga} pairs was first proposed in order to explain the occurrence of a broad luminescence band at approximately 1100 nm (1.12 eV) in n-doped GaAs (Williams 1968). But the final prove of the existence of these vacancy complexes was provided by a series of positron annihilation lifetime measurements, in which vacancy concentrations could be measured directly (Gebauer et al. 1997, Gebauer et al. 1999). It is commonly assumed that both $Si_{Ga}V_{Ga}$ and $Te_{As}V_{Ga}$ are two times negatively charged, as one would expect for the complex consisting of a singly positive donor and triply negative V_{Ga}. The charge of a gallium vacancy in n-type GaAs was determined in a theoretical study (Baraff and Schlüter 1985) and in a recent positron work (Gebauer et al. 2003). The same charge state (-2e) for vacancy-complexes in both silicon- and tellurium-doped GaAs was found to be consistent with the compensation model based on results of electrical measurements in these materials and with the model of self-activated luminescence developed for the interpretation of the results of luminescence experiments in n-doped GaAs (Williams and Mackintosh 1968). As one can see, structure and electronic properties of $Si_{Ga}V_{Ga}$ and $Te_{As}V_{Ga}$ seem to be very similar. However, results of temperature-dependent positron annihilation measurements in GaAs:Si and GaAs:Te turned out to be quite different.

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[1] Defects in GaAs:Si are discussed in details in Section 3.

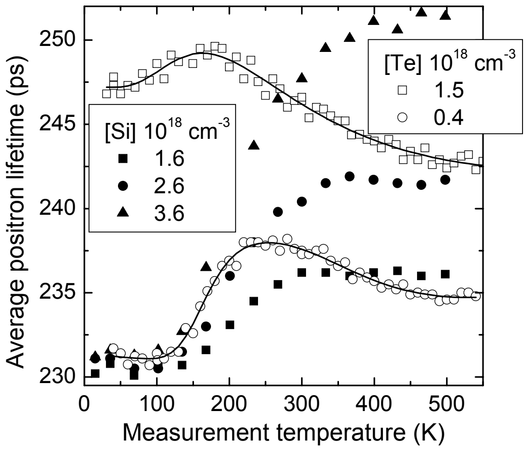

Fig. 7.1: *Average positron lifetime as a function of measurement temperature for as-grown Si- and Te-doped GaAs. The data for GaAs:Te are taken from (Gebauer et al. 2003)*

Fig. 7.1 shows average positron lifetime measured as a function of temperature in GaAs doped with different doses of tellurium (solid symbols) or silicon (open symbols). The data corresponding to GaAs:Si were obtained in this work (Fig. 4.2). Positron lifetime results in GaAs:Te originate from the PhD work of J. Gebauer (Gebauer 2000) and were published in Refs. (Gebauer et al. 1997; Gebauer et al. 2003). In both materials, average positron lifetime measured at room temperature is distinctly higher than the bulk lifetime of GaAs, indicating positron trapping into vacancy-like defects. The trapping rate, which can be determined from τ_{av} with the Eq. 3.6, increases to higher doping levels, indicating thereby the increase of the vacancy-like defect concentration. The decrease of τ_{av} to low temperatures indicates positron trapping by shallow traps represented by acceptor-like ions (e.g. C_{As} or Cu_{Ga}). In GaAs:Si, silicon doping itself is a source of Si_{As}-acceptors. Therefore, shallow traps concentration is always higher, and thus the decrease of τ_{av} is more pronounced in in Si-doped than in Te-doped GaAs. The shallow trap defects have a considerable influence on positron trapping at temperatures $\leq$ 300 K. At higher temperatures, positron detrapping from the weak Coulomb potential of negative ions dominates and positron annihilation at shallow traps can be neglected. Thus, the behavior of τ_{av} at $T \geq 300$ K is governed by positron trapping into vacancy like defects and is the subject of interest for the following discussion.

In Te-doped GaAs, τ_{av} continuously decreases with increasing temperature (Fig. 7.1). Such $\tau_{av}(T)$ behavior was also often observed in positron annihilation lifetime studies of GaAs (e.g., in intentionally undoped GaAs (Krause-Rehberg and Leipner 1999) or in electron-irradiated GaAs (Polity et al. 1997)) and other semiconductors (e.g., in neutron irradiated silicon). According to theoretical trapping model (Section 3.2.1), a decrease of the positron trapping coefficient, and consequently a decrease of τ_{av}, is expected for a negative vacancy (Fig. 3.5). This is in agreement with the assumed negative charge state for the $Te_{As}V_{Ga}$ complex. The validity of the trapping model is corroborated by the good fit of the experimental data (solid lines in fig. 7.1) according to the two-defect trapping model considering negative vacancies and shallow trap defects (Section 3.2.2). However, the model was found to be inapplicable for interpretation of $\tau_{av}(T)$ curves in Si-doped GaAs.

As fig. 7.1 shows, lifetime measurements in GaAs:Si reveal no decrease of the average positron lifetime in the high-temperature region. This is surprising, since one expected the same $\tau_{av}(T)$ dependence as in GaAs:Te due to the equal charge states of the vacancy-defects in these materials. But in contrast to GaAs:Te, τ_{av} in GaAs:Si remains constant or even slightly increases at temperatures above room temperature. Such $\tau_{av}(T)$ behavior is considered to be characteristic for a neutral, not a negative vacancy (Fig. 3.5). All attempts to apply the model of positron trapping by negative vacancies and shallow traps to the results obtained for GaAs:Si ended in failure. The best possible fit yielded unreasonably high concentrations of acceptor-like defects – two orders of magnitude higher than the vacancy concentration. This is obviously just a mathematical artifact. The $\tau_{av}(T)$ represent a competitive process of positron trapping into vacancy and shallow trap defects. In order to produce the $\tau_{av}(T)$ dependence similar to the one measured in GaAs:Si, the $T^{-1/2}$ increase of the trapping rate of negative vacancy, K_v and K_R in Eq. 3.15, must be compensated by positron trapping into shallow trap defects (Fig. 3.7) up to the temperatures of 600 K. For this, the positron detrapping rate (δ_{st} in Eq. 3.16) must be reduced by increasing the shallow trap concentration, C_{st}.

Thus, it was shown that the model of positron trapping into a negative vacancy is inconsistent with the results of positron lifetime measurements in GaAs:Si. There are two possible explanations of this disagreement:

1) The theoretical considerations of the temperature dependence of positron trapping are correct and thus $Si_{Ga}V_{Ga}$-complex must be neutral;
2) $Si_{Ga}V_{Ga}$ is negative. In this case, the theory must be reconsidered.

7.2 Positron trapping in GaAs doped with Si and Te simultaneously

7.2.1 Experimental

The samples investigated were cut from a GaAs single crystal doped with silicon and tellurium atoms simultaneously (GaAs:Si&Te). The crystal was grown using VGF-technique and characterized by means of chemical analysis (AtES – atom emission spectroscopy) and electrical measurements (Hall-effect) at FCM. AtES measurements revealed large variation of the dopants concentration over the crystal length. Therefore, five samples were taken from different axial positions of the crystal for positron annihilation investigations. In the following, the samples are referred according to their position with integers 1-5, whereas 1 and 5 correspond to the ingot seed and tail, respectively.

Despite large concentration gradients of Si- and Te- donors, free electron density was found to be nearly the same in all samples pointing to high electrical compensation in this material. The results of SIMS and Hall-effect measurements for three of samples are summarized in Table 7.1.

Table 7.1 – *Dopant and free electron concentrations and electron mobility measured in the GaAs:Si&Te samples investigated in this work*

Sample #	**[Si] (cm^{-3})**	**[Te] (cm^{-3})**	**n (cm^{-3})**	**μ (cm^2/Vs)**
1	1.5×10^{17}	9.3×10^{17}	9.37×10^{17}	3116
4	2.0×10^{17}	1.0×10^{18}	1.19×10^{18}	2481
5	9.0×10^{17}	8.5×10^{18}	1.27×10^{18}	1556

Temperature-dependent positron annihilation lifetime measurements were performed according to the general measurement procedure (Section 3.4) on the experimental setup with time-resolution of 241 ps.

7.2.2 Results of temperature-dependent PALS measurements

Results of two-component analysis of the lifetime spectra obtained for GaAs:Si&Te samples at different measurement temperatures are shown in fig. 7.2. The decomposition was successful only for high-temperature spectra ($T > 300$ K), while for the lower temperatures large scattering of the fitting parameters, defect-related lifetime τ_d and its intensity, was observed [fig. 7.2 (a)]. Obviously at low temperatures, positron trapping into more than one defect occurs and hence the one-defect (two-component) trapping model can not be applied. However, it was impossible to decompose the spectra into more than two components. This indicates the small difference between positron lifetimes corresponding to the different types of positron traps. Due to the small difference, the individual lifetimes could not be separated. Thus, positrons trapped by negative ions (shallow positron traps) annihilate within the same time period as those annihilating from the bulk. At higher temperatures, positrons were trapped predominantly by a defect with $\tau_d = 265 \pm 5$ ps [fig. 7.2 (a)]. In GaAs, positron lifetimes of this order are attributed to a monovacancy-type defect [calculation]. Note that the same defect-related lifetime was obtained also for GaAs:Si (Chapter 4).

The average positron lifetime reveals complicated temperature and doping dose dependence [fig. 7.2 (b)]. The lowest τ_{av} is observed in the sample #1 doped with the smallest numbers of Si and Te atoms. $\tau_{av}(T)$ curve demonstrates a plateau at about 234 ps in 500 K – 330 K temperature region, increases as temperature decreases from 330 K down to 200 K and decreases with the further lowering of the measurement temperature. The latter decrease is ascribed to positron trapping into shallow trap defects as discussed for GaAs:Si in section 4.2.2. the two next samples #2 and #3 demonstrate a $\tau_{av}(T)$ behavior qualitatively similar to that of #1. The only difference is the shift of the τ_{av} to higher

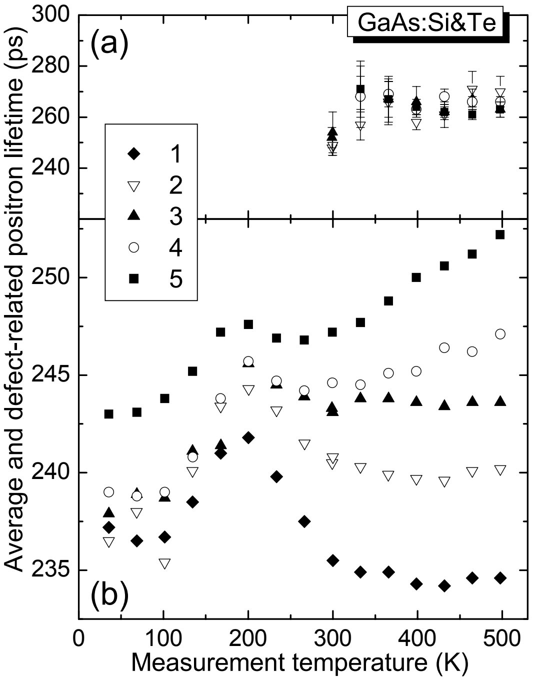

Fig. 7.2: *Results of the temperature-dependent positron lifetime measurements obtained in GaAs doped with Si and Te atoms.*

(a) defect-related lifetime;

(b) average positron lifetime.

values that is especially remarkable in the high-temperature region, where the influence of shallow positron traps is negligibly small. One should also note the extension of the plateau interval down to 300 K in sample #3. The enhancement of the average positron lifetime values to higher doping levels corresponds to an increase of the vacancy-like defects concentration. This tendency is also preserved for the last two samples #4 and #5. However, there are no plateau-regions observed for these specimens. Instead, τ_{av} demonstrates a continuous increase in high-temperature interval, giving rise to the minimum in the $\tau_{av}(T)$ function at the temperature of about 270 K.

7.2.3 Discussion

The temperature dependence of the positron trapping in GaAs:Si&Te represents an important result enlarging significantly the state of our knowledge on positron trapping in semiconductors and also on point defects in heavily n-doped GaAs. There were three main conclusions made: (i) the temperature behavior of τ_{av} cannot be explained in terms of two-defect trapping model assuming positron capture by negative ions (shallow traps) and open-volume defects (vacancies). Hence, (ii) there are more than one vacancy-type defects present in GaAs:Si&Te crystals. It is the first time, that the presence of more than one monovacancy-like defects in a single sample can be unambiguously demonstrated by PALS measurements. This is possible due to the different temperature behavior of positron trapping coefficient corresponding to these defects. (iii) The results support the assumption of different defect properties of Si- ant Te-doped GaAs. The conclusions stated above are based on the following arguments:

(i) Inconsistence of two-defect model.

The following reasons often used for interpretation of τ_{av} T-dependence were found to be ***not*** applicable:

1) *Competitive trapping into negative vacancy-like defects and shallow positron traps.* At best, this is demonstrated by $\tau_{av}(T)$ curves measured in samples #4 and #5 (Fig. 7.2). The two extremes observed at 200 K and 270 K cannot be modeled principally under the assumption of a single open-volume positron trap.
2) *Temperature-induced change of defect charge state.* Due to the high doping range, 10^{18}-10^{19} cm^{-3} (Table 7.1), the Fermi level position in all samples was in the conduction band and could not be significantly affected by the temperature change in the interval of 300-500 K concerned here. Hence, no recharging effect could have taken place.
3) *Electron screening effect*, which can change the effective charge of defects felt by positrons and lead to a different temperature dependence of τ_{av} in differently doped samples. However, the free electron concentration was found to be nearly the same in all samples (Table 7.1). Thus the screening effect in sample #5 cannot be much larger than that in sample #1 to explain the profound difference in $\tau_{av}(T)$.

(ii) Presence of several types of open-volume defects.

4) Consequently, more than one kind of vacancy-like defects should exist in the crystal. The positron trapping into these defects has a different temperature dependence resulting in the complex behavior of $\tau_{av}(T)$ observed.
5) The positron lifetimes related to these defects could not be separated, i.e. have similar values. Hence, the defects must of a similar type. The found defect-related lifetime τ_d=264 ps corresponds to a monovacancy in GaAs.
6) It is the first time the simultaneous presence of such defects is observed in a semiconducting crystal by positrons.

(iii) Consequences for Si- ant Te-doped GaAs:

7) Obviously, the defect causing the increase of τ_{av} with increasing temperature (samples #4 and #5) must dominate positron trapping in the heavily-doped GaAs:Si. In GaAs:Te, in contrast, the other defect type is the dominating positron trapping center which demonstrates a strong decrease of the average positron lifetime towards higher temperatures. The superposition of positron trapping into the two defect types results in the temperature dependence $\tau_{av}(T)$ in GaAs:Si&Te.
8) A possible explanation for the different temperature dependence of positron trapping demonstrated by these defects is their different charge states. According to theoretical calculations (Section 3.2.1) increase of τ_{av} with increasing temperature is expected for

the neutral (or positive!) vacancy, while decreasing τ_{av} corresponds to trapping by the negative vacancy.

The latter item represents the subject of discussion for the following subsection.

7.3 Systematization of results

The results presented in the previous section have clearly demonstrated that the temperature dependence of positron trapping contains important information about the defect configuration in the GaAs crystals doped with Si or Te. In this section, the features of the $\tau_{av}(T)$ curves obtained for a great variety of samples studied in this work are examined in details. Most of the experimental data originated from the study of VCz-grown GaAs (Chapter 6). Therefore, it is reasonable to consider in the first place the lifetime spectra presented in that chapter. As far as vacancy-like defects are the subject of interest, only the high temperature (T>200 K) part of $\tau_{av}(T)$ have to be considered. At temperatures below 200 K, positron trapping into shallow traps can not be neglected and dominates the temperature behavior of .τ_{av}. As the main parameter, the slope of a $\tau_{av}(T)$ curve will be discussed. For the sake of convenience, a special designation for the parameter has been introduced:

$$Y = \frac{d}{dT} \tau_{av}(T) \tag{7.1}$$

Let's call *Y* the temperature decay of τ_{av}.

In a first approximation, the *Y* estimation could be done just by the fitting of the increasing part of the τ_{av} curves with a simple linear function. Surprisingly, such rather qualitative analysis performed for each sample revealed a presence of three *discreet* temperature decays (linear slopes) of the average positron lifetime. In other words there were three different temperature dependencies of τ_{av} observed, as demonstrated by the example $\tau_{av}(T)$ curves in Fig. 7.3. Y_1 is represented by two curves, corresponding to the samples

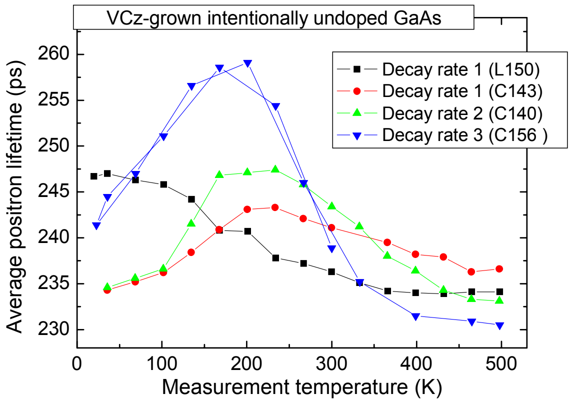

Fig. 7.3: *Three typical temperature dependences of the average positron lifetime found in intentionally undoped GaAs. The lines are drawn to guide the eye.*

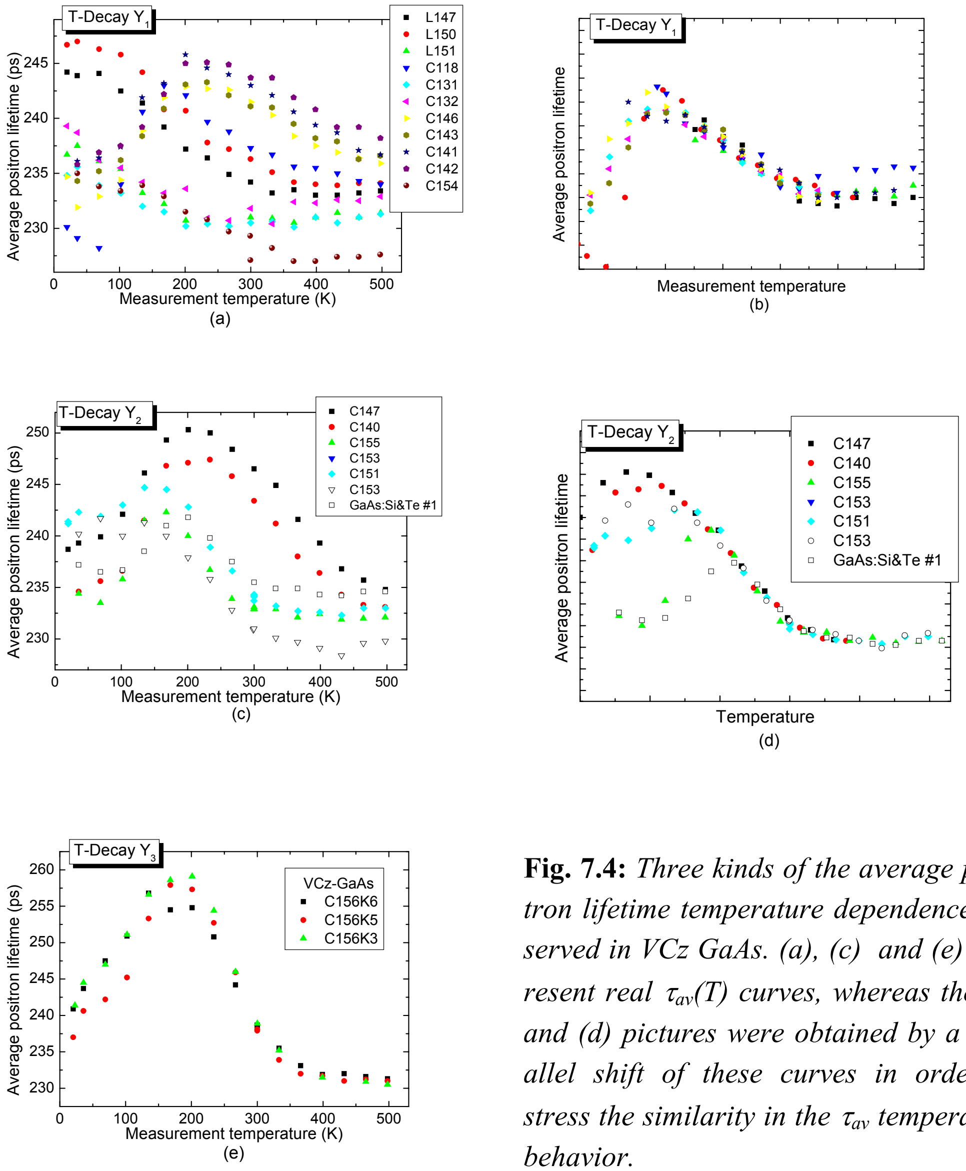

Fig. 7.4: *Three kinds of the average positron lifetime temperature dependence observed in VCz GaAs. (a), (c) and (e) represent real $\tau_{av}(T)$ curves, whereas the (b) and (d) pictures were obtained by a parallel shift of these curves in order to stress the similarity in the τ_{av} temperature behavior.*

with (red symbols) and without (black symbols) shallow traps. Fig. 7.4 shows the existence of the *discreet* decays more clearly. Parts (a), (c) and (e) present “real” τ_{av} curves related to Y_1, Y_2 and Y_3 respectively. The (b) and (d) parts were constructed manually with the help of a simple parallel shift of the measurement curves in order to make the similarity of their temperature slopes obvious. The decay Y_3 was observed only in three samples cut from the same crystal (C156).

Similar analysis was performed for the results obtained in the other samples investigated in this work. It turned out, that all the samples can be classified in four groups according to the kind of temperature τ_{av} temperature dependence (Table 7.2). Most of the investigated samples belong to the first group, for which τ_{av} demonstrates the smallest decay (Y_1) – 3 to 4 ps per temperature increase of 100 K. For the samples of the group II,

Table 7.2 –*GaAs crystals investigated in this work grouped according to the temperature decays of* $\tau_{av}(T)$*. The numbers in the column captions correspond to the change of the value of* τ_{av} *per 100 K*

I (0.03-0.04 ps)	**II (0.07-0.08 ps)**	**III (0.17-0.19 ps)**	**IV T-independent**
L147	C147	C156 (K3, K6, K9)	**Heavily-doped GaAs:Si** Sections 4.2 and 4.3
L150	C140		
L151	C153		
C118	C155		
C131	C151		
C132	**GaAs:Si&Te #1**		
C146			
C143			
C141			
C142			
C155			
C154			
GaAs:Si (Section 4.4)			
SI annealed GaAs (Section 5.2.2)			

τ_{av} decreases faster, at the rate of 7-8 ps/100 K. But the highest temperature decay was observed for the three samples of group 3 and amounted to 17-19 ps per 100 K.

The occurrence of the discrete decay rates was never reported before (at least, such reports are not known to the author). Such behavior of τ_{av} was also not predicted by theoretical calculations. It seems to be a completely new experimental observation.

There are three possible explanations of the observed four kinds of temperature dependences:

1) different types of the vacancy-like defects responsible for positron trapping;
2) different concentrations of the vacancy and/or shallow trap defects;
3) different charge states of the vacancy defects.

The first two variants are hardly probable. Firstly, there are only *two* principle vacancy types in GaAs – gallium and arsenic vacancies – and *three* different decay rates. Naturally, the vacancies can form complexes with other intrinsic or extrinsic point defects, such as impurity atoms or antisites, which could have different positron trapping coefficients. But it is hardly possible, that the same defect complex is formed in very different GaAs samples of the group I and group II, which have different concentrations of impurities and free charge carriers and even different conductivity type. The second vari-

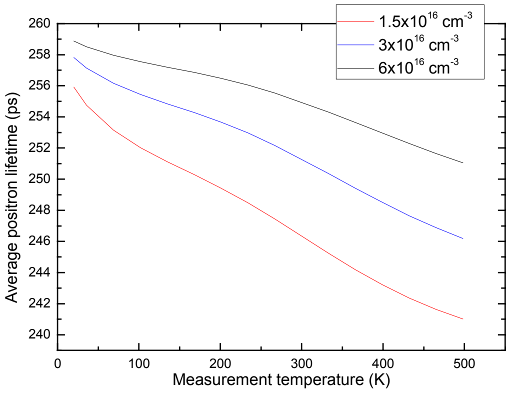

Fig. 7.5: *Average positron lifetime calculated as a function of temperature for different vacancy concentrations. One-defect trapping model was used. Trapping into a negative vacancy was assumed.*

ant must be also discarded as inappropriate, since it is rather improbable that the ratio between the concentrations of vacancy and shallow trap defects would amount to constant, moreover discrete values in order to explain the occurrence of only three slopes. Moreover, according to the theoretical model described in section 3.2, the vacancy concentration does not influence the slope of the $\tau_{av}(T)$ curve that much. This is demonstrated in Fig. 7.5 with the help of simulation of the $\tau_{av}(T)$ curves for the case of positron trapping by a single defect-type, negative vacancy, presented in different concentrations. As can be seen, concentration variations in the range of observed vacancy concentrations are not strong enough to cause the remarkable changes in the decay rate. Even if it was, we would end up with a continuous distribution of the slopes of the $\tau_{av}(T)$ curves due to continuous distribution of the concentrations of vacancies and shallow traps in investigated samples. This was not observed. More probable, the variation of the vacancy concentrations leads to a parallel vertical shift of the whole $\tau_{av}(T)$ curve which can be clearly seen for some of the samples (e.g., L147 and L150 of group I; C147 and C140 of group 2).

The third variant is the most reasonable one. Obviously, each discrete $\tau_{av}(T)$ decay rate corresponds to a specific defect configuration of studied crystal. The question is: which defect property can vary in a discrete way? This can be only the charge state. However, theoretical calculations (Section 3.2.1) did not predict different temperature dependences of the positron trapping rate for single and double negative vacancies. In contrary, for both vacancies charge states the same $T^{-1/2}$ dependence of the positron trapping rate should be expected (Fig. 3.5). This is in direct contradiction to the experimental results obtained in this work. It is the author's opinion, that the present theoretical model of positron capture does not correctly describe the temperature dependence of the process of positron trapping and must be reconsidered. The improvement of the model will allow to extract much more information from the results of temperature dependent positron lifetime measurements concerning the microstructure of the detected positron trapping centers.