

Positron-trapping mechanism at grain boundaries

C. Hidalgo and N. de Diego

Departamento de Física del Estado Sólido, Facultad de Ciencias Físicas, Universidad Complutense, 28040 Madrid, Spain

F. Plazaola

Laboratory of Physics, Helsinki University of Technology, SF-02150 Espoo, Finland

(Received 28 November 1984)

Positron trapping at grain boundaries has been observed in fine-grained samples of Zn—0.123 wt. % Al—0.063 wt. % Mg by positron-lifetime measurements. Positron trapping at precipitates was also found. The temperature dependence of the positron-trapping rate shows that the positron-trapping mechanism at grain boundaries and precipitates is diffusion controlled, where the positron diffusion constant is proportional to $T^{-1/2}$. No evidence of detrapping is observed in this alloy.

I. INTRODUCTION

Much effort is being made at present to study the temperature dependence of positron trapping at different kinds of defects. Particularly, strong interest has arisen concerning the temperature dependence of the trapping rate since this is an important parameter that can provide useful information about the defect concentration. The behavior of the trapping rate as a function of temperature can help on the other hand to understand the trapping processes at different kinds of defects. Many experimental works dealing with the temperature dependence of the trapping rate have been published and several mechanisms for explaining the experimental results have been proposed. A temperature dependence of positron trapping at voids has been observed by Petersen *et al.*¹ and by Nieminen *et al.*² in aluminum, and by Schultz *et al.*,³ Hyodo *et al.*,⁴ and Pagh *et al.*⁵ in molybdenum. Positron diffusion, thermal detrapping from shallow traps, and positron reflection at the surfaces of the voids are some of the mechanisms suggested for explaining the temperature dependence of the trapping processes at voids. Smedskjaer *et al.*⁶ have proposed a mechanism of thermal detrapping from dislocations but no detrapping from jogs that would act as positron-trapping sites with a higher binding energy than the dislocation core itself. This model has been applied by Pagh *et al.*⁵ to interpret the results obtained in irradiated molybdenum containing voids and dislocation loops.

Grain boundaries are also expected to act as trapping sites for positrons but there are only a few experimental works in the literature dealing with the positron-grain boundary interaction. Room-temperature measurements performed in a fine-grained Zn-Al alloy⁷ and more recently in Fe alloys^{8,9} and in a Zn-Al-Mg alloy¹⁰ seem to indicate that grain boundaries are capable of trapping positrons. Detrapping processes have been suggested for grain boundaries¹¹ to interpret the results obtained at low temperature by Rice-Evans *et al.*¹² A diffusion picture could be reasonable, since grain boundaries are extended defects; under this assumption the trapping rate κ is proportional

to the diffusion constant D ,¹³ whose dependence with the temperature should be $D \propto T^{-1/2}$ when phonon scattering is dominant.¹⁴ Under these circumstances the trapping rate temperature dependence would be the same.

The purpose of this work is to understand the nature of the trapping processes at grain boundaries by studying the temperature dependence of the positron-trapping rate in a fine-grained Zn-Al-Mg alloy. We have performed the measurements for the extremes of a very fine and a very large grain size, where the trapping signal of positrons interacting with grain boundaries is not detectable.

In Sec. II the experimental details are given; Sec. III is dedicated to describing the results obtained for both large-grained (Sec. III A) and fine-grained samples (Sec. III B); in Sec. IV the experimental results are discussed; finally a brief summary of conclusions is included in Sec. V.

II. EXPERIMENTAL

The fine-grained Zn—0.123 wt. % Al—0.063 wt. % Mg alloy was prepared by reverse rolling at the Technical University of Braunschweig;¹⁵ the starting material was in the form of a sheet, 1 mm thick, with a grain size of 0.7 μm ; larger grains were achieved by giving the samples different thermal treatments; the grain size was estimated by the intercept method using electron and optical microscopy. In all cases the dislocation density seemed to be sufficiently low to assume no significant trapping signal originated from dislocations.¹⁶ Table I lists the thermal treatments and the measured grain sizes for the three specimens studied. Well-annealed Zn (99.999% pure) specimens were also available for comparison.

Positron-lifetime spectra were measured in the temperature range 77–320 K by using a fast coincidence system, having a resolution of 270 ps full width at half maximum. As positron emitter a normal ²²Na source was used, made by evaporating an aqueous ²²NaCl solution onto a titanium foil (0.89 mg cm⁻²). The fraction of positrons annihilating in the titanium foil was estimated to be about 7%.¹⁷

TABLE I. Thermal treatments and measured grain sizes for the three studied specimens.

Sample	Thermal treatment	l (μm)
A	3 h at 520 K (N_2 atmosphere)	~ 100
B	0.5 h at 380 K (vacuum)	~ 1
C	as received	~ 0.7

The component due to annihilations in the salt and to surface effects was obtained by studying the spectrum of a well-annealed Zn sample, in which only one component due to free annihilations is expected. After Ti-foil correction the spectra could be decomposed into two components characterized by two different lifetimes: $\tau_1 = 154$ ps (bulk lifetime in Zn at room temperature) and $\tau_2 = 510$ ps. This long component of faint intensity ($\sim 2\%$) was attributed to salt and surface effects and was subtracted from the spectra in the final analysis.

For specimen A additional equilibrium measurements were performed above room temperature up to 480 K in steps of 20 K. The specimen was then allowed to cool and a new measurement was carried out at room temperature; further thermal treatments were given to this specimen by immersing it in a liquid-nitrogen bath for several hours. A positron-lifetime spectrum was collected at room temperature after each thermal treatment at 77 K.

Lifetime spectra were analyzed using a computer program very similar to Positronfit.¹⁸ By means of this program the lifetimes τ_i , the corresponding intensities I_i , and the average lifetime $\bar{\tau} = \sum_i \tau_i I_i$, were calculated.

III. RESULTS

A. Large-grained samples

The lifetime spectra were analyzed by using a two-component decomposition, which gave a satisfactory fit to the experimental data. In Fig. 1 the two components obtained, τ_1 and τ_2 , the average lifetime $\bar{\tau}$, and the longer-component intensity I_2 have been plotted as a function of the temperature.

Figure 1 was formed from two runs, one from 77 to 300 K and the other from 300 to 480 K. After the first run the specimen was cooled down and measured at 77 K; afterward, it was again measured at 300 K continuing with the second run. The positron-lifetime results obtained during the measurements in between the two runs were the same as those obtained previously in the first run. This indicates that the part of the curve corresponding to the measurements between 77–300 K is reversible. However, after finishing the second run of measurements, a new measurement at 300 K showed a positron average lifetime 10 ps shorter indicating the nonreversibility of the high-temperature part of the curve.

It can be seen from Fig. 1 that within its statistical accuracy the longer component seems to be independent of temperature with a mean value $\tau_2 = 230$ ps. The intensity I_2 increases with decreasing temperatures below room temperature and shows also a drastic increase for temperatures above 380 K, which is attributed to the creation of thermal vacancies. The observed trapping signal below

380 K cannot be due to trapping at grain boundaries, since the grain size ($l \sim 100 \mu\text{m}$) is too large to give a measurable intensity. This long component, $\tau_2 = 230$ ps, has also been reported in a previous work¹⁰ for the same alloy in measurements performed at room temperature. Since the τ_2 value is close to the lifetime of positrons trapped at vacancies in Zn [$\tau_b \sim 220$ ps (Ref. 19)], this component has been attributed to the presence of Mg-atom-vacancy complexes or incoherent matrix-precipitate interfaces.¹⁰

In order to clarify the nature of these traps, further thermal treatments were given to this specimen by immersing it in a liquid-nitrogen bath for several hours as described in Sec. II. After each treatment a lifetime spectrum was collected at room temperature; satisfactory fits were obtained by making a two-component analysis, where the longer component τ_2 had a value of about 230 ps. In order to reduce the statistical scatter, the long component was fixed to its average value $\tau_2 = 230$ ps; the results are shown in Fig. 2, which is a plot of the positron-lifetime parameters $\bar{\tau}$, τ_1 , and I_2 against the time the specimen spent immersed in the liquid nitrogen bath. The point marked I in the figure gives the values of the parameters measured at room temperature before annealing at higher temperatures; after annealing about 50 h at temperatures up to 480 K the most remarkable feature is the decrease of the longer-component intensity which drops to about 9% (point marked 0 h at 77 K in Fig. 2). An in-

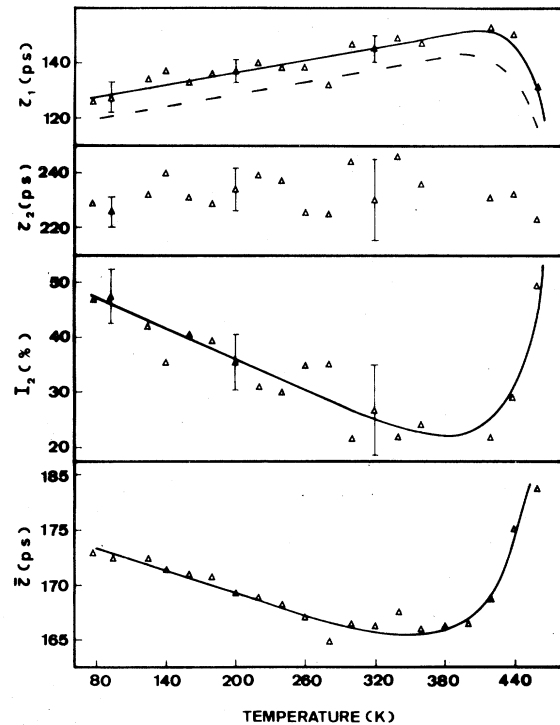


FIG. 1. Positron-lifetime parameters as a function of the temperature in the Zn-0.123 wt. % Al-0.063 wt. % Mg alloy ($l \sim 100 \mu\text{m}$). The bars correspond to statistical deviation from the fit. The dashed line for τ_1 has been drawn from the trapping model by assuming the presence of only one kind of trap.

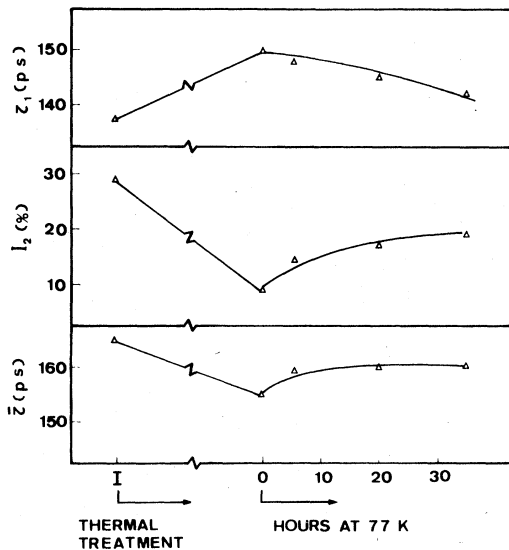


FIG. 2. Evolution of the positron lifetime parameters in the Zn-0.123 wt. % Al-0.063 wt. % Mg ($l \sim 100 \mu\text{m}$) for different thermal treatments (see text for explanation).

crease in I_2 is observed after a treatment of 5 h at 77 K; the intensity increases for longer treatments at 77 K. This behavior is readily understood if the defects responsible for the observed trapping component are assumed to be precipitates. A prolonged heat treatment at high temperatures would dissolve part of the precipitates giving a small intensity for the trapping component at room temperature; the reprecipitation process takes place when the samples are cooled at 77 K stimulating an increase in I_2 . The lifetime value of $\tau_2 = 230$ ps suggests positron trapping at incoherent matrix-precipitate interfaces or at defects inside them.²⁰

The dashed line shown in Fig. 1 has been deduced from the simple trapping model assuming that only one kind of positron trap, characterized by a lifetime, $\tau_2 = 230$ ps, is present in the sample; under this hypothesis the value for the shorter component τ_1 is given by²¹

$$\tau_1 = \frac{\tau_f}{1 + \kappa\tau_f}, \quad (1)$$

κ being the value of the trapping rate for a trap described by a lifetime τ_2 ,

$$\kappa = I_2(\Lambda_1 - \Lambda_2), \quad (2)$$

where Λ_1 , Λ_2 , and I_2 are the decay rates and intensity respectively that can be obtained from a deconvolution analysis of an observed positron-lifetime spectrum; τ_f is in the Zn positron bulk lifetime. We notice that the model fits the experimental results reasonably and thus it can be concluded that the interfaces or defects associated with precipitates are the only traps responsible for the observed behavior in specimen A.

B. Fine-grained samples

A two-component analysis gave satisfactory fits for both samples C and B in the temperature range studied. The longer-lifetime component was basically independent of the sample temperature and had an average value of

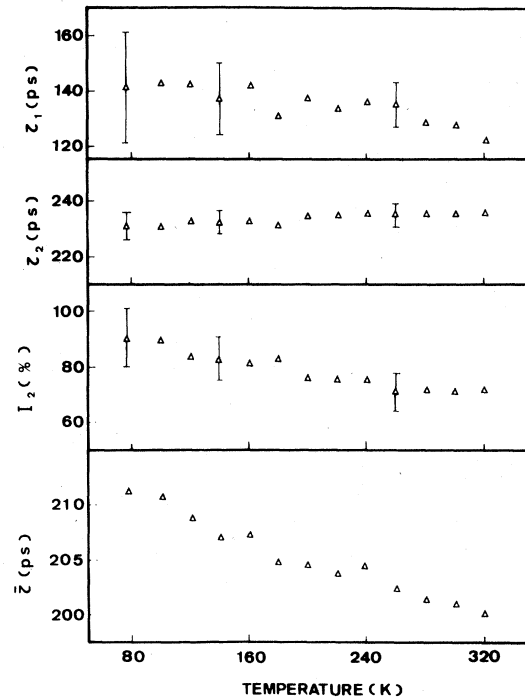


FIG. 3. Positron lifetime parameters as a function of the temperature in the Zn-0.123 wt. % Al-0.063 wt. % Mg alloy ($l \sim 0.7 \mu\text{m}$).

234 ps. A final analysis was performed constraining the τ_2 value to its average, 234 ps, in order to reduce the statistical scatter. Figures 3 and 4 give the positron parameters τ_1 , τ_2 , $\bar{\tau}$, and I_2 for both samples C ($l \sim 0.7 \mu\text{m}$) and B ($l \sim 1 \mu\text{m}$), respectively. In Fig. 3 the results of a free analysis are shown; Fig. 4 presents the results obtained by

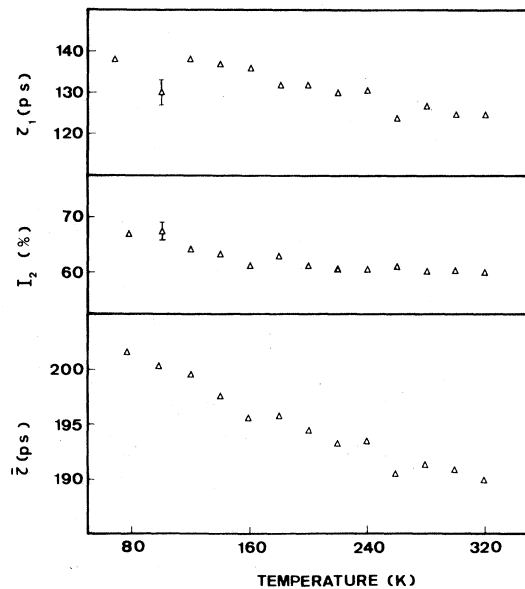


FIG. 4. Positron lifetime parameters as a function of the temperature in the Zn-0.123 wt. % Al-0.063 wt. % Mg alloy ($l \sim 1 \mu\text{m}$). The long component τ_2 has been fixed to $\tau_2 = 234$ ps.

fixing $\tau_2=234$ ps. The intensity I_2 , the mean lifetime $\bar{\tau}$, and the shorter lifetime τ_1 are observed to increase with decreasing sample temperature in both cases; the values of $\bar{\tau}$ and I_2 are higher than the measured ones for the larger-grained alloy. This means that some other traps are acting in addition to incoherent precipitates; following the ideas presented in a previous work¹⁰ the predominant traps for fine-grained specimens would be grain boundaries.

IV. DISCUSSION

From the present experiments it can be seen that the annihilation parameters are strongly dependent on the temperature in the alloy. Current ideas for explaining this temperature dependence observed in many materials include the presence of shallow traps and the diffusion model. Diffusion-limited trapping is probably a good approximation for defects extended in two or three dimensions such as grain boundaries, incoherent precipitates, and large voids. In this case the trapping rate is proportional to the diffusion constant D ;¹³ when phonon scattering dominates, the dependence of the diffusion constant D with the temperature should be $D \propto T^{-1/2}$.¹⁴

We have calculated the temperature dependence of the trapping rate κ for the sample A ($l \sim 100 \mu\text{m}$) in the range 77–300 K by using the one-trap model [expression (2) in which $\Lambda_2 (\equiv 1/\tau_2)$ has been fixed by using $\tau_2=230$ ps]. The results are plotted in Fig. 5. As it can be seen, the trapping rate at the precipitates exhibits a temperature dependence $\kappa \propto T^{-(0.44 \pm 0.04)}$, clearly indicating that the trapping mechanisms at the precipitates are controlled by diffusion processes with the phonon scattering dominating. It is seen²² that the positron-impurity scattering does not play any role at these temperatures.

When interpreting the results obtained for fine-grained samples the influence of grain boundaries must also be taken into account. The main problem is to understand the increase in the shorter component τ_1 when the temperature decreases. We can consider two possible arguments to explain the observed behavior.

(i) Grain boundaries contain shallow traps for positrons; since the lifetime associated with shallow traps is close to

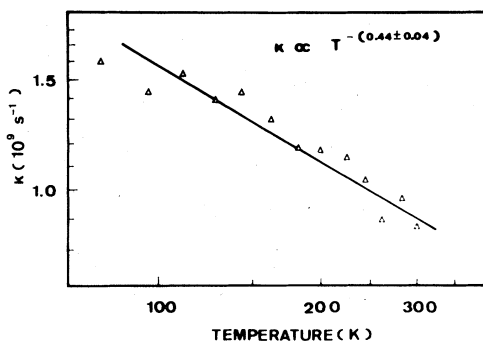


FIG. 5. The trapping rate to the precipitates in the Zn–0.123 wt. % Al–0.063 wt. % Mg alloy ($l \sim 100 \mu\text{m}$) as a function of the temperature.

the bulk lifetime, the presence of such traps could affect only the short component τ_1 , leading to an increase in τ_1 , due to the annihilation of an increasing number of positrons from the shallow traps for decreasing temperatures.

(ii) Grain boundaries are characterized by two different lifetimes: $\tau_2 \approx 234$ ps, which corresponds to a vacancylike defect, and τ'_2 , between the above mentioned $\tau_2 \approx 234$ ps and the bulk lifetime $\tau_f = 154$ ps, i.e., $\tau_f < \tau'_2 < \tau_2$; the lifetime τ'_2 corresponds to trapping at zones of low atomic density associated with grain boundaries with an electron density higher than the one associated with a vacancy. The influence of this τ'_2 component is seen mainly on the τ_1 component, whose increase for decreasing temperatures should be due to the increase of the positron diffusion length.

McKee *et al.*⁷ observed in a Zn–Al alloy, a long-lifetime component of 250 ps that they attribute to grain boundaries since no other kind of defect was present in their samples; however for grain sizes lower than $1.5 \mu\text{m}$, there is disagreement between the simple trapping model and their experimental value of the short-lifetime component τ_1 . The observed disagreement increases for decreasing grain sizes; for grain sizes higher than $1.5 \mu\text{m}$, the simple trapping model agrees with their experimental data.

The same behavior of τ_1 observed in a Zn–Al alloy has also been observed in the present alloy.¹⁰ Figure 6 shows the evolution of τ_1 , measured at room temperature after annealing the sample with an initial grain size of about $0.7 \mu\text{m}$ (point A) during 30 min at steps of about 10 K from 360 to 425 K; the dashed line corresponds to the values deduced from the experimental results by assuming the existence of only one kind of trap. This hypothesis is reasonable because the lifetimes for both grain boundaries and precipitates are quite similar and thus they can be treated as if they were the same trap. It can be observed that the discrepancy between the experimental τ_1 values and the value deduced from the trapping model is higher for annealing temperatures below 390 K (i.e., when the grain size is sufficiently small to give an appreciable contribution). For temperatures above 390 K, an appreciable

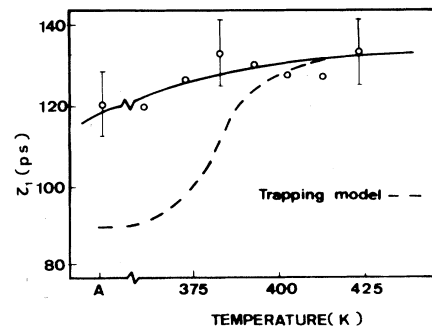


FIG. 6. Evolution of the short component τ_1 measured at room temperature in the Zn–0.123 wt. % Al–0.063 wt. % Mg alloy as a function of annealing temperature. The point marked A corresponds to the values in the as-received materials; for temperatures above 390 K an appreciable grain growth is observed (see Ref. 10). For the dashed line drawn for τ_1 see Fig. 1 caption.

grain-size increase takes place.

These remarks suggest the necessity of postulating the existence of two different traps for positrons associated with grain boundaries. Thus, we should consider only the second hypothesis; on the other hand, it has to be pointed out that the systematic increase observed for τ_1 is difficult to explain by only assuming the presence of shallow traps.

Since the lifetime associated with grain-boundary zones having the lowest atomic density is very similar to the trapping component associated with precipitates and since both trapping mechanisms are diffusion controlled, both contributions can be treated, from the mathematical point of view, as if they were only one component.

We shall then deduce the temperature dependence of the trapping rate for samples having small grain size by assuming the following.

(a) Grain boundaries can be described by two kinds of defects capable of trapping positrons characterized by two lifetimes (τ_2, τ_2') given by

$$\tau_2 \approx 234 \text{ ps}, \quad \tau_f < \tau_2' < \tau_2.$$

(b) The detrapping mechanisms are negligible for both kinds of defects in the temperature range studied (77–320 K).

(c) The trapping-rate temperature dependence for both defects is

$$\kappa \propto T^{-\alpha},$$

where α represents an adjustable parameter.

It is clear that if the assumptions (a) and (b) are fulfilled then $\alpha \approx 0.5$. In this way the value deduced for α from the experimental results is a test for the validity of the proposed assumptions.

The expression for the average lifetime obtained from the trapping model by using the above assumptions is given by²¹

$$\bar{\tau} = \frac{1 + \kappa_2' \tau_2' + \kappa_2 \tau_2}{\lambda_f + \kappa_2' + \kappa_2}, \quad (3)$$

κ_2' and κ_2 being the trapping rates into the defects characterized by τ_2' and τ_2 lifetimes, respectively.

The expression (3) can also be written as

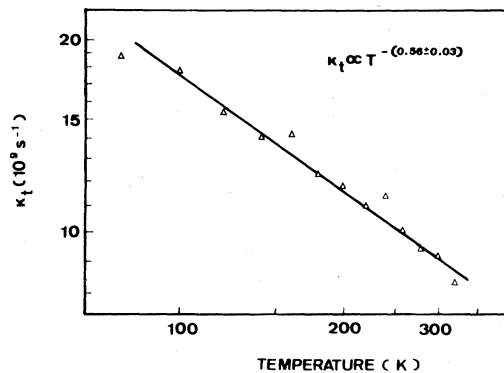


FIG. 7. The trapping rate $\kappa_t = \kappa_2' + \kappa_2$ as a function of the temperature in a Zn–0.123 wt. % Al–0.063 wt. % Mg alloy ($l \sim 0.7 \mu\text{m}$).

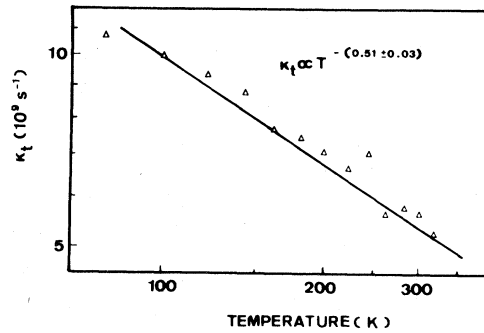


FIG. 8. The trapping rate $\kappa_t = \kappa_2' + \kappa_2$ as a function of the temperature in a Zn–0.123 wt. % Al–0.063 wt. % Mg alloy ($l \sim 1 \mu\text{m}$).

$$\bar{\tau} = \frac{1 + \tau_2(\kappa_2 + \kappa_2') - \kappa_2'(\tau_2 - \tau_2')}{\lambda_f + \kappa_2' + \kappa_2}. \quad (4)$$

From hypothesis (a) it follows that $\tau_2 - \tau_2' < \tau_2$; moreover, $I_2 > I_1$, then $\kappa_2' < \kappa_2$.²³ Thus the expression (4) can be approximated to

$$\bar{\tau} \approx \frac{1 + \tau_2(\kappa_2 + \kappa_2')}{\lambda_f + (\kappa_2 + \kappa_2')}. \quad (5)$$

From expression (5) we obtain finally

$$\frac{\kappa_2 + \kappa_2'}{\lambda_f} \approx \frac{\tau_f - \bar{\tau}}{\bar{\tau} - \tau_2}. \quad (6)$$

By using expression (6) and the experimental results, we have calculated $\kappa_t = \kappa_2 + \kappa_2'$. The variation of κ_t with the temperature is shown in Figs. 7 and 8 for the samples C and B, respectively. In the plots, the variation of τ_f with the temperature has been taken into account. For a well-annealed Zn sample, $\Delta\tau_f/\tau_f$ has been found experimentally to be 2.6×10^{-2} between 77 and 300 K. It can be seen that the κ_t temperature dependence is given by

$$\kappa_t \propto T^{-(0.56 \pm 0.03)} \quad l \sim 0.7 \mu\text{m},$$

$$\kappa_t \propto T^{-(0.51 \pm 0.03)} \quad l \sim 1 \mu\text{m}.$$

As the value of the adjustable parameter α is in both cases in good agreement with a diffusion picture, i.e., $\alpha \approx 0.5$, it can be concluded that hypotheses (a) and (b) are correct. Therefore no evidence of shallow traps associated with grain boundaries has been found in the Zn–0.123 wt. % Al–0.063 wt. % Mg alloy.

V. CONCLUSION

The positron experiments performed in a fine-grained Zn–Al–Mg alloy lead to the following conclusions.

(i) By studying the evolution of the lifetime with the temperature, we have demonstrated that the temperature dependence of the trapping rate at grain boundaries and incoherent matrix-precipitate interfaces or defects inside them can be described by

$$\kappa \propto T^{-1/2}.$$

This means that the trapping mechanisms at grain boundaries and precipitates are diffusion controlled with phonon scattering dominant, i.e., $D \propto T^{-1/2}$.

(ii) It has been proved that grain boundaries contain two kinds of traps for positrons, one is characterized by a lifetime which is close to that for vacancies in Zn ($\tau_2 = 234$ ps) and the second one is characterized by a lifetime τ'_2 ($154 \text{ ps} < \tau'_2 < 234 \text{ ps}$), which can be described as a zone having an electronic density higher than the one associated with a vacancy.

(iii) No evidence of detrapping from shallow traps associated with grain boundaries has been found in the Zn-0.123 wt. % Al-0.063 wt. % Mg alloy.

ACKNOWLEDGMENTS

We are most grateful to P. Hautojärvi and A. Vehanen for helpful discussions and to H. Müller for supplying the samples. One of us (F.P.) would like to thank the Eusko Jurlaritz for financial support.

-
- ¹K. Petersen, N. Thrane, G. Trumpy, and R. W. Hendricks, *Appl. Phys.* **10**, 85 (1976).
²R. M. Nieminen, J. Laakkonen, P. Hautojärvi, and A. Vehanen, *Phys. Rev. B* **19**, 1397 (1979).
³P. J. Schultz, K. G. Lynn, I. K. MacKenzie, Y. C. Jean, and C. L. Snead, Jr., *Phys. Rev. Lett.* **44**, 1629 (1980).
⁴T. Hyodo, R. J. Douglas, R. Grynszpan, B. T. A. McKee, and A. T. Stewart, *J. Phys. F* **13**, 573 (1983).
⁵B. Pagh, H. E. Hansen, B. Nielsen, G. Trumpy, and K. Petersen, *Appl. Phys. A* **33**, 255 (1984).
⁶L. C. Smedskjaer, M. Manninen, and M. Fluss, *J. Phys. F* **10**, 2237 (1980).
⁷B. T. A. McKee, G. J. C. Carpenter, J. F. Watters, and J. R. Schultz, *Philos. Mag. A* **41**, 65 (1980).
⁸C. Hidalgo and N. de Diego, *Phys. Status Solidi A* **80**, K145 (1983).
⁹C. Hidalgo, N. de Diego, and M. A. Ochando, *Phys. Status Solidi A* **83**, K93 (1984).
¹⁰C. Hidalgo, N. de Diego, and M. A. Ochando, *Solid State Commun.* **49**, 611 (1984).
¹¹I. K. MacKenzie, *Phys. Rev. B* **16**, 4705 (1977).
¹²P. Rice-Evans, T. Hlaing, and I. Chaglar, *Phys. Rev. Lett.* **37**, 1415 (1976).
¹³A. Seeger, *Phys. Lett.* **40A**, 135 (1972).
¹⁴B. Bergersen, E. Pajanne, P. Kubica, M. J. Stott, and C. H. Hodges, *Solid State Commun.* **15**, 1377 (1974).
¹⁵H. Müller and F. Hässner, *Scr. Metall.* **15**, 487 (1981).
¹⁶B. T. A. McKee, S. Saimoto, A. T. Stewart, and M. J. Stott, *Can. J. Phys.* **52**, 759 (1974).
¹⁷M. Bertolaccini and L. Zappa, *Nuovo Cimento B* **52**, 487 (1967).
¹⁸P. Kirkegaard and M. Eldrup, *Comput. Phys. Commun.* **7**, 401 (1974).
¹⁹P. Moser (private communication).
²⁰G. Dlubek, O. Brümmer, P. Hautojärvi, and J. Yli-Kaupilla, *Philos. Mag. A* **44**, 239 (1981).
²¹R. N. West, *Positrons in Solids*, edited by P. Hautojärvi (Springer, Berlin, 1979), p. 89.
²²R. M. Nieminen, in *Proceedings of the LXXXIII International School of Physics "Enrico Fermi"*, edited by W. Brandt and A. Dupasquier (Academic, New York, 1983), p. 359.
²³A. Vehanen, P. Hautojärvi, J. Johansson, J. Yli-Kaupilla, and P. Moser, *Phys. Rev. B* **25**, 762 (1982).