PHYSICAL REVIEW B VOLUME 37, NUMBER 16 1 JUNE 1988

Positron annihilation study of deformed silver

I. Lemahieu, D. Segers, L. Dorikens-Vanpraet, M. Dorikens, and Motoko-Kwete*
Laboratory for Nuclear Physics, Positron Centre, Proeftuinstraat 86 9000 Gent, Belgium

(Received 31 August 1987; revised manuscript received 21 January 1988)

Positron annihilation Doppler-broadening parameters were measured on deformed silver. Deformations were carried out at liquid-nitrogen temperature and at room temperature. From annealing studies it was seen that stage-II and stage-III defects have a profound influence on the positron annihilation parameters. Measurements below room temperature of Ag annealed at room temperature revealed a strong temperature dependence of the positron annihilation parameters, which could be explained by trapping of positrons in shallow traps. The location of the annealing stage for dislocations depends upon the deformation temperature and upon the degree of deformation.

I. INTRODUCTION

In recent years, positrons have proved to be very sensitive probes for the investigation of defects in metals. Trapping of positrons has been seen at monovacancies, vacancy clusters, and dislocations, and the ability of the positrons to distinguish between those defects has contributed to make the positron annihilation technique a valuable tool in the studies of defects and their properties (e.g., formation and migration energies, recovery stages, etc.)[1] By plastic deformation of metals dislocations and point defects are introduced. If the deformation is performed at a temperature below the stage for migration of vacancies the defects are retained in the sample. During isochronal annealing a recovery stage for the migration of intrinsic point defects can be observed. In the past several authors have suggested the possibility of trapping (and detrapping) of positrons in shallow traps,[2–6] either from a theoretical point of view or as an explanation for experimental results. Only very recently, however, the first direct evidence for the existence of shallow traps was given by positron annihilation lifetime measurements in Ag deformed at room temperature.[7,8] As far as we know this was also one of the first positron annihilation studies on deformed silver reported in the literature.

In this work we present positron annihilation Doppler-broadening measurements on silver deformed at room temperature and at liquid-nitrogen temperature.

II. EXPERIMENTAL

The material used was 99.999%-pure polycrystalline silver of Koch & Light. Samples with a well-known thickness were prepared and chemically polished. Before the deformation the samples were annealed in a vacuum of 10^{-4} Pa for 8 h at a temperature of 1050 K. The samples were compressed under liquid nitrogen and at room temperature. The samples compressed under liquid nitrogen were deformed to different degrees of thickness reduction, i.e., 30% and 56%. For the deformation at room temperature the thickness reduction was 30%. After the deformation a ^{22}Na source deposited on a 7.5 μm Kapton foil was mounted between the samples. For the samples deformed under liquid nitrogen the same source was mounted between the samples under liquid nitrogen. The sample-source assembly was placed in a self-built cryostat. The mounting of the samples deformed under liquid nitrogen was done very carefully, so that the temperature never rose above 80 K. The measuring temperature in the cryostat could be varied between 77 K and 700 K. A temperature stability better than 0.5 K was obtained through a PID regulation system. The temperature was monitored with a platinum-100 resistor.

The Doppler broadening of the annihilation line was measured. The energy calibration of the multichannel analyzer was 0.050 keV per channel. The resolution of the system was 1.15 keV for the 514 keV gamma line of ^{85}Sr at a count rate of 8×10^3 counts per second.

The whole measuring system (temperature controller and multichannel analyzer) was controlled with the help of a PC/XT. The measuring time was 55 min. After each measurement the data were transferred to floppy disk and during a supplementary 5 min a new temperature was set and the system was allowed to reach temperature stabilization. After suitable background correction[9] the annihilation line was characterized by an S parameter,[10] calculated over a window of 31 channels or 1.55 keV.

III. RESULTS AND DISCUSSION

Figure 1 represents the results for the isochronal annealing of the samples deformed at liquid nitrogen temperature to a thickness reduction of 30%. During a first run the isochronal annealing was measured increasing the temperature in steps of 10 K from 80 K to 680 K and again decreasing the temperature to 80 K. It was noticed that below room temperature a structure occurs in the S-parameter data. Above 340 K a huge decrease in the S-parameter value occurs, which is attributed to the annealing of dislocations introduced during deformation. The complete behavior of the isochronal annealing curve was exactly reproduced during a second run on samples deformed to the same thickness reduction.

In order to obtain some information on the tempera-

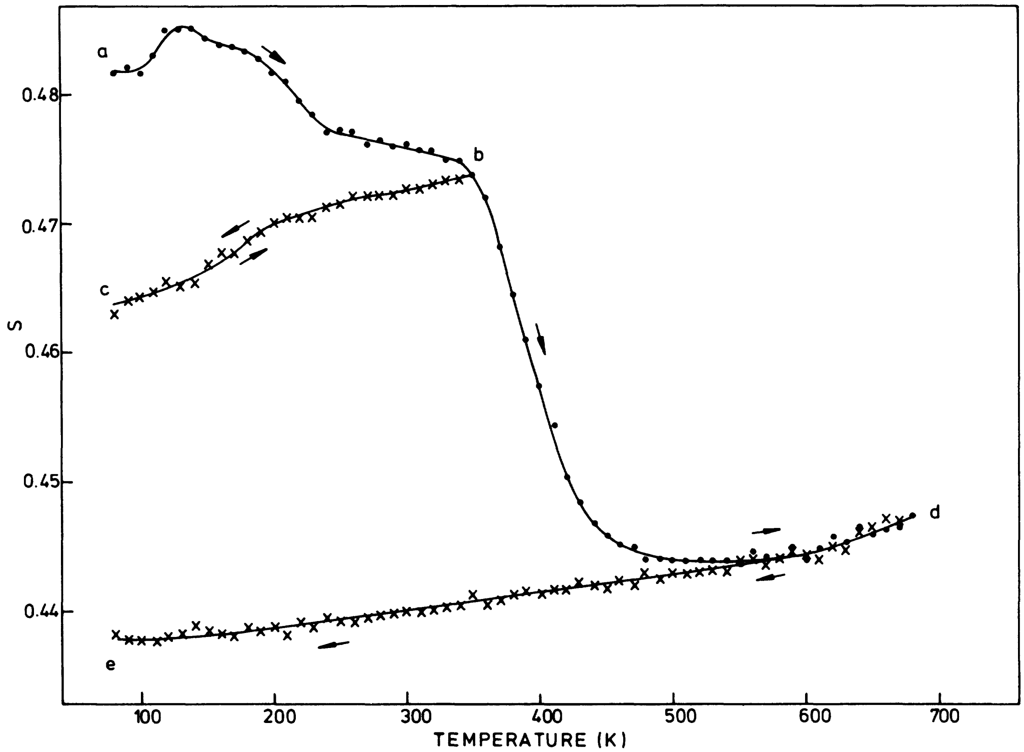

FIG. 1. Positron annihilation S parameter as a function of the annealing temperature for silver samples deformed at liquid-nitrogen temperature to a thickness reduction of 30%. *b*-*c* of the curve was measured after annealing at 340 K and represents the temperature behavior when mainly dislocations are present. The solid line through the data points is a visual fit to guide the eye. *d*-*e* of the curve represents the effect of thermal expansion.

ture dependence of the positron annihilation parameters when the samples mainly contain dislocations, we planned a third run on another set of samples also deformed to 30% thickness reduction. The results of this third run are represented in Fig. 1. After isochronal annealing at 340 K (*a*-*b* in Fig. 1) the temperature was then first lowered to 80 K (*b*-*c*) and subsequently again increased from 80 K to the final annealing temperature at 680 K (*c*-*d*). After the final annealing at 680 K the temperature was again lowered to 80 K in order to measure the temperature dependence of the positron behavior in the annealed samples (*d*-*e*). The behavior of the annealing curve coincided completely with the results obtained during the two previous runs.

From Fig. 1 we see that an important trapping effect of about 7.5% occurs in silver after deformation at liquid-nitrogen temperature. Between 80 and 100 K the S-parameter value is fairly constant. From 100 K on, an increase in the S-parameter value is seen. After annealing at 120 K the line-shape parameter value decreases to reach a more flat region between 250 and 340 K. The most important annealing stage is located between 340 and 420 K. Above 560 K an increase in the S-parameter value is seen. From the literature[11] we know that positron trapping in thermally induced vacancies is noticeable from 770 K on. After annealing at 680 K the S parameter was measured decreasing the temperature (*d*-*e* in Fig. 1). In that part of the curve not much structure is seen. The solid line through these data points represents the behavior of the S parameter due to thermal expansion effects. A polynomial of the 4th degree was fitted to the thermal expansion data.[12] The S-parameter behavior was taken proportional to the thermal expansion data, i.e.,

$$S=S_0+\beta(\Delta l/l_0) \tag{1}$$

with

$$\Delta l/l_0=aT+bT^2+cT^3+dT^4\ . \tag{2}$$

The proportionality constant β was found to be 0.77.

The huge stage between 340 and 420 K is attributed to the annealing of dislocations.[13] Branch *b*-*c* of Fig. 1, measured at descending temperatures after annealing at 340 K, represents the temperature dependence of the positron annihilation parameters when mainly dislocations are present.

In Fig. 2 we represent the recovery results for samples deformed at liquid-nitrogen temperature to a thickness reduction of 56%. At these deformations saturation trapping in the introduced defects is expected.[14,15] The annealing behavior is very similar to the one seen in Fig. 1. The trapping effect immediately after deformation at liquid-nitrogen temperature is more important (9%) than in the sample deformed to a thickness reduction of 30%. For the 56%-deformed samples the annealing stage for dislocations occurs at a somewhat lower temperature.

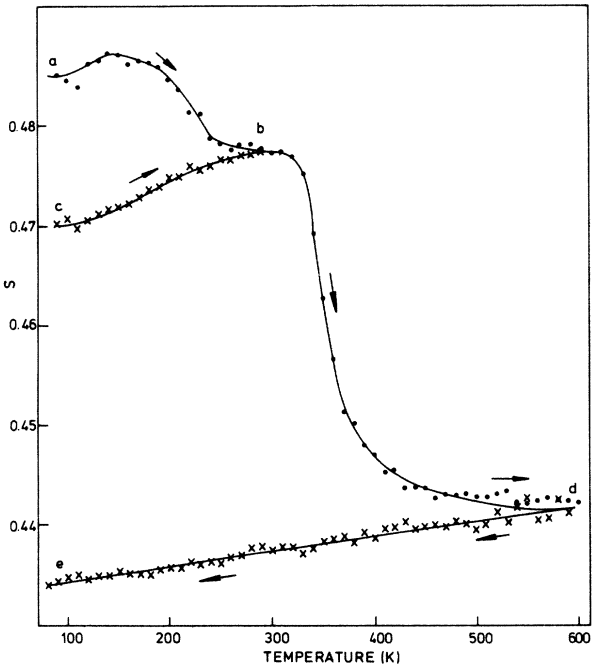

FIG. 2. Positron annihilation S parameter as a function of the annealing temperature for silver samples deformed at liquid-nitrogen temperature to a thickness reduction of 56%. b-c of the curve was measured after annealing at 300 K and represents the temperature behavior when mainly dislocations are present.

The annealing stage itself is in the beginning also steeper. After annealing at 300 K the S parameter was measured downwards in temperature (b-c in Fig. 2). The same behavior as in Fig. 1 is observed.

When we consider the positron annihilation S parameter measured at descending temperatures, after annealing at 340 K (for 30%-deformed Ag—see Fig. 1) or at 300 K (for 56%-deformed Ag—see Fig. 2), it is obvious that between 80 and 280 K the temperature dependence is much stronger than can be expected from thermal expansion effects. Between 280 and 340 K the slope of c-b in Figs. 1 and 2 flattens out, and becomes equal to the slope of the S parameter in thermal equilibrium (e-d of the curves).

Similar results obtained by positron annihilation Doppler-broadening measurements on deformed copper[16] were first explained in terms of a temperature-dependent trapping rate. In this case, the two-stage trapping model results in

$$S(T)=PS_t+(1-P)S_f \tag{3}$$

with

$$S_f=S_{f0}+\alpha_f T$$

the S parameter for the free annihilation,

$$S_t=S_{t0}+\alpha_t T$$

the S parameter for the trapped positrons, and α_f,α_t temperature coefficients to incorporate thermal expansion effects. The fraction of positrons P trapped at annihilation is given by

$$P=\frac{\mu(T)C/\lambda_f}{1+\mu(T)C/\lambda_f}\ , \tag{4}$$

where $\mu(T)$ is the temperature-dependent trapping rate, C the concentration of the defects, and $1/\lambda_f$ the positron lifetime.

This explanation is, however, not sufficient to describe our experimental results. For the heavily deformed Ag samples (Fig. 2), saturation trapping in the introduced defects is expected,[14,15] and in that case Eq. (3) becomes

$$S(T)=S_t(T)=S_{t0}+\alpha_t T\ . \tag{5}$$

As the only temperature dependence in Eq. (5) is due to thermal expansion effects, and this is in contradiction with the experimental results, it is concluded that the two-state trapping model with a temperature-dependent trapping rate cannot describe the results in an adequate manner.

An alternative interpretation for the temperature dependence below room temperature after annealing at 300 K is the trapping of positrons in shallow traps. At the lowest temperatures there is a competition between trapping in shallow and deep traps. As the temperature is increased, detrapping becomes important and the positrons escaping from the shallow traps are localized by the deep traps, so that an increase in the S parameter with increasing temperature can be observed. The Doppler-broadening measurements on deformed Cu (Ref. 16) were explained by MacKenzie[2] in a similar way.

This interpretation is in accordance with the recent findings of Linderoth *et al.*[7,8] for room temperature deformed silver. From lifetime measurements they concluded that there was clear evidence that shallow positron traps are present in Ag deformed at room temperature to a thickness reduction of 8%. It was seen that below 100 K the trapping probability becomes sufficiently high to allow most positrons to be in a trap, shallow or deep, when annihilating. At more elevated temperatures the shallow traps are depleted and the deeper traps become the dominant annihilation sites. The annihilation characteristics in the shallow traps were found to be very close to these of the free positrons. The binding energy of the positrons to the shallow traps according to Linderoth *et al.*[7,8] is 9 meV. From our measurements it is not possible to calculate an exact value for the binding energy of the positrons to the shallow traps. An upper limit for this binding energy can be estimated from the relation[17]

$$\Delta\varepsilon=kT\ln(\tau_t kt/h)\ , \tag{6}$$

where $\Delta\varepsilon$ is the binding energy, k is Boltzmann's constant, h is Planck's constant, and T is the absolute temperature. τ_t is the lifetime of the positron trapped in the shallow trap, which is 136 ps according to Linderoth.[7,8] When we take $T=280$ K as the temperature where detrapping becomes dominant, then a value $\Delta\varepsilon=0.16$ eV is obtained. If, on the other hand, a value $T=100$ K is put into Eq. (6), as this is the temperature where detrapping becomes important according to Linderoth *et al.*,[7,8] a value $\Delta\varepsilon=0.05$ eV is obtained as an upper limit for the

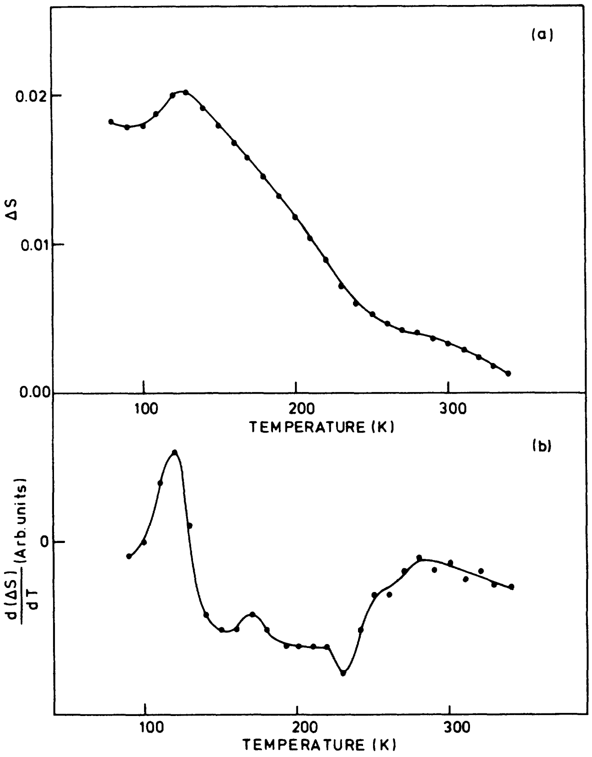

FIG. 3. (a) Difference curve of *a*-*b* and *b*-*c* of Fig. 1. This curve represents the trapping of positrons in stage-II and stage-III defects. The solid line through the data ponts is a visual fit to guide the eye. (b) Derivative of the difference curve of part (a).

binding energy.

To see the effect of positron trapping in point defects introduced during the deformation of the 30%-deformed samples, a difference curve was calculated from the results of the direct isochronal annealing curve (Fig. 1 *a*-*b*) and the curve after isochronal annealing at 340 K measured downwards in temperature (Fig. 1 *b*-*c*). The result is represented in Fig. 3(a). If the point defects annealing out below room temperature agglomerate to form dislocation rings, then the *S*-parameter value obtained after annealing at 340 K is not solely due to the trapping of positrons in deformation induced dislocations. An additional trapping effect in defects created by the agglomeration then occurs. This means that under those circumstances the differential curve does not exactly represent the portion of trapping of the positrons in point defects introduced during the deformation (since the part that is subtracted is constituted not only of trapping in dislocations but also in dislocation rings formed by the agglomeration of point defects). This means that the differential curve represents the lower limit of positron trapping in the point defects introduced during the deformation at liquid nitrogen temperature.

From Fig. 3(a) it is seen that an important trapping effect results. The solid line through the data points represents a visual fit to the data. To obtain some more information on the occurrence of the annealing stages, the derivative of the solid line was calculated. The result is represented in Fig. 3(b). A maximum occurs at 120 and 170 K. A small minimum is seen around 230 K. From the literature we know that stages II and III are located below room temperature (see Ref. 13 and references therein). Stage II recovery occurs in the temperature range from 95 to 170 K and is divided into three substages. Stage III annealing occurs in a very broad recovery stage from 170 to 270 K. We believe that the maxima seen in Fig. 3(b) at 120 and 170 K are connected to the annealing of stage-II defects, while the structure in the temperature interval 190 to 280 K has to be attributed to the annealing of stage-III defects.

No clear-cut explanation for the annealing of stage-II defects has been given in the literature. Several possible explanations are considered for the stage-II mechanism,[13] i.e., (i) release of impurity trapped interstitials, (ii) recombination of close interstitial-vacancy pairs, (iii) annealing of divacancies or larger vacancy clusters, (iv) rearrangement of dislocations, (v) rearrangement within point defect strings, and (vi) migration or breakup of di-interstitials or larger interstitial agglomerates. From our measurements we cannot decide which of the above mechanisms are responsible for the observed effect. We can only conclude that stage-II defects affect the positron annihilation characteristics and that some substructure in the stage-II annealing can be observed.

It has been seen in the literature that after heavy deformation stage III is not governed by a single activated process.[18] In strongly deformed metals the number of dislocations is so high that they act as the main sinks and that the mutual interaction of point defects becomes less important. This means that the stage-III annealing can be very complicated. From our Doppler-broadening measurements we indeed see that the stage in Fig. 3(b) between 170 and 270 K is complicated. Lifetime measurements could provide supplementary information on the possible annealing mechanisms.

Figure 4 represents the results of Doppler-broadening measurements on room temperature deformed silver to a thickness reduction of 30%. Immediately after the deformation the *S* parameter was measured below room temperature (*a*-*b*-*c* in Fig. 4). When comparing this part of the curve with the results of Figs. 1 and 2, we see that the temperature behavior is the same.

Afterwards the samples were isochronally annealed above room temperature (*c*-*d* in Fig. 4) up to 680 K, and then the *S* parameter was measured downwards in temperature (*d*-*e* in Fig. 4). It was seen that the effect due to pure thermal expansion (*d*-*e*) completely coincides with the curve measured in the low-temperature deformed samples.

It was also seen that the annealing stage for dislocations in the room temperature deformed samples appears at higher temperatures (between 400 and 500 K) and that the slope is not so steep as in the low-temperature deformed samples, although the degree of deformation is the same as for the low-temperature deformed samples of Fig. 1. When comparing these results with those of Linderoth *et al.*,[7,8] who had deformed silver at room temperature to a thickness reduction of only 8%, it can be

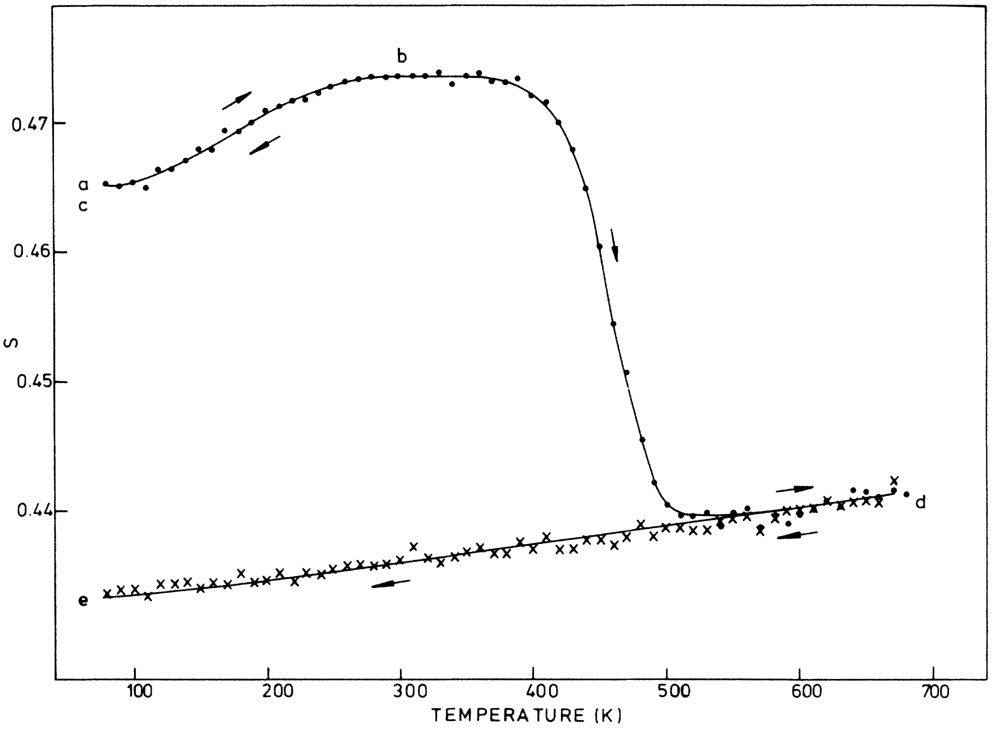

FIG. 4. Positron annihilation S parameter as a function of the annealing temperature for silver samples deformed at room temperature to a thickness reduction of 30%. a-b-c of the curve was measured immediately after the deformation and represents the temperature behavior when mainly dislocations are present. The solid line through the data points is a visual fit to guide the eye. d-e of the curve represents the effect of thermal expansion.

seen that there the temperature at which the dislocations anneal out (above 500 K) is even higher than in our measurements. It can be concluded that the temperature at which the recovery stage for dislocations appears strongly depends on the degree of deformation and on the deformation temperature. The recovery takes place at lower temperatures with increasing degree of deformation, and takes place at higher temperatures with increasing deformation temperature. Similar results were previously found by positron annihilation measurements in deformed Al.[19,20]

IV. CONCLUSIONS

From the Doppler-broadening measurements it was seen that:

(i) stage-II and stage-III defects do trap positrons;

(ii) there is a pronounced annealing stage for dislocations;

(iii) the temperature dependence below room temperature of the positron annihilation parameters for samples mainly containing dislocations can be explained by the presence of shallow traps;

(iv) the occurrence and the shape of the annealing stage for dislocations is a function of the degree of deformation and depends on the deformation temperature.

ACKNOWLEDGMENTS

This work is part of the research program of the IIKW Brussels, Belgium. We would like to thank the technical staff of the laboratory for their assistance, especially M. Dupont for his help in the maintenance of the self-built cryostat. We would also like to thank S. Linderoth and C. Hidalgo for having made available their paper before publication. Financial support from IIKW, Brussels, is acknowledged.

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*On leave from Université de Kinshasa, Zaire.

[1] *Positron Solid-State Physics*, edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983).

[2] I. K. MacKenzie, Phys. Rev. **16**, 4705 (1977).

[3] P. J. Schultz, K. G. Lynn, I. K. MacKenzie, Y. C. Jean, and C. L. Snead, Phys. Rev. Lett. **44**, 1629 (1980).

[4] P. J. Schultz, PhD. thesis, University of Guelph, Ontaria, Canada, 1981.

[5] P. J. Schultz, I. K. MacKenzie, K. G. Lynn, R. N. West, and C. L. Snead, in *Proceedings of the 6th International Conference on Positron Annihilation, Texas*, edited by P. G. Coleman, S. C. Sharma, and L. M. Diana (North-Holland, Am-

sterdam, 1982), p. 458.

[6] R. Nieminen, see Ref. 1, p. 359.

[7] S. Linderoth, PhD. thesis, Lyngby University, Denmark, 1987.

[8] S. Linderoth and C. Hildago, Phys. Rev. B **36**, 4054 (1987).

[9] D. Segers, L. Dorikens-Vanpraet, M. Dorikens, D. Vandenbroucke, and C. Platteau, see Ref. 5, p. 900.

[10] I. K. MacKenzie, J. A. Eady, and R. R. Gingerich, Phys. Lett. **33A**, 279 (1970).

[11] W. Luhr-Tanck, Th. Kurschat, and Th. Hehenkamp, Phys. Rev. B **31**, 6994 (1985).

[12] *American Institute of Physics Editorial Handbook,* 3rd ed., edited by Dwight E. Gray (McGraw-Hill, New York, 1972), Part 4.

[13] A. Van den Beukel in *Vacancies and Interstitials in Metals,* edited by A. Seeger, D. Schumacher, W. Schilling, and J. Diehl (North-Holland, Amsterdam, 1970), p. 427.

[14] C. Dauwe, D. Segers, L. Dorikens-Vanpraet, and M. Dorikens, Phys. Status Solidi (A) **17**, 443 (1973).

[15] D. Segers, M. Dorikens, and L. Dorikens-Vanpraet, in *Proceedings of the 7th International Conference on Positron Annihilation, New Delhi,* edited by P. C. Jain, R. M. Singru, and K. P. Gopinathan (World-Scientific, Singapore, 1985), p. 564.

[16] P. Rice-Evans, T. Hlaing, and I. Chaglar, Phys. Rev. Lett. **37**, 1415 (1976).

[17] A. Seeger, J. Phys. F **3**, 248 (1973).

[18] H. I. Dawson, Acta Metall. **13**, 453 (1965).

[19] B. Nielsen and K. Petersen, (unpublished).

[20] K. Petersen, PhD. thesis, Lyngby University, Denmark, 1978.