



**Thermal behavior and range distribution of  $^{209}\text{Bi}$  implanted into the Al/V bilayer structure**

C. A. Olivieri, M. Behar, P. L. Grande, P. F. P. Fichtner, F. C. Zawislak, J. P. Biersack, and D. Fink

Citation: *Journal of Applied Physics* **63**, 4431 (1988); doi: 10.1063/1.340161

View online: <http://dx.doi.org/10.1063/1.340161>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/63/9?ver=pdfcov>

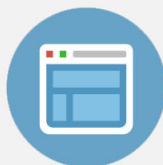
Published by the [AIP Publishing](#)

---



## Re-register for Table of Content Alerts

Create a profile.



Sign up today!



# Thermal behavior and range distribution of $^{209}\text{Bi}$ implanted into the Al/V bilayer structure

C. A. Olivieri,<sup>a)</sup> M. Behar, P. L. Grande, P. F. P. Fichtner, and F. C. Zawislak  
*Instituto de Física, Universidade Federal do Rio Grande do Sul, 90049 Porto Alegre, RS, Brazil*

J. P. Biersack and D. Fink  
*Hahn-Meitner-Institut, D-1000 Berlin, West Germany*

(Received 7 July 1987; accepted for publication 2 December 1987)

350-keV  $^{209}\text{Bi}^+$  was implanted into an Al (1000 Å)/V bilayer system. The Bi depth distribution measured by Rutherford backscattering agrees well with predictions obtained via the Monte-Carlo simulation method (TRIM code). Diffusion coefficients for Bi in both the V substrate of the Al/V system and the pure V foil are extracted after thermal annealings in a temperature range between 200 and 700 °C. The results show that the Bi ions follow a hindered diffusion at the Al film of the Al/V bilayer and for temperatures higher than 580 °C diffuse regularly in the V bulk.

## I. INTRODUCTION

The present study is related to the distribution of implanted Bi ions at the interface region of the bilayer system composed by a film of Al deposited on V substrate (Al/V). This work is the continuation of a systematic investigation initiated with the Al/Ti (Ref. 1) and Al/KCl (Ref. 2) systems, which was undertaken with three major aims. First, to enlarge the few experimental available data, which up to now mainly deal with insulator/semiconductor and semiconductor/semiconductor systems and second, to compare the experimental results with the latest theoretical prediction. Recently, a new version of the Monte-Carlo simulation method (TRIM code<sup>3</sup>) has been applied in order to predict among other properties the entire range distribution of implanted ions into bilayer structures.<sup>1,2,4</sup> Finally, we are also concerned with the thermal behavior of the implanted ions into bilayer structures, to understand the mechanism by which the implanted ions diffuse in these kinds of systems.

In previous works<sup>1,2</sup> studying the Al/Ti and Al/KCl bilayer systems implanted with Bi ions, we have found two major features. First, there is a very good agreement between the experimental results and the latest theoretical TRIM predictions. Second, when the systems are annealed up to 500 °C most of the implanted ions are trapped at the interface region. Hence, it is of interest to see if this retarded diffusional behavior is a peculiarity of the above two systems or if it is a general property of bilayer structures. With these purposes, we have undertaken the present work, where we have implanted  $^{209}\text{Bi}^+$  ions, both into a double-layer system, composed by an Al film deposited onto a V foil and into a pure V foil. Both samples have been isochronally annealed in order to compare the corresponding thermal diffusion behavior. All depth profiles have been analyzed using the Rutherford backscattering technique (RBS).

## II. EXPERIMENTAL PROCEDURE

The Al/V sample was prepared at the HMI, Berlin, evaporating a film of pure Al of 1000 Å thickness onto a chemically cleaned V foil (Marz grade) at a pressure of  $10^{-6}$ – $10^{-7}$

Torr. The Al/V and V samples were implanted at room temperature with 350- and 250-keV  $\text{Bi}^+$  ions, respectively, at the 400-keV HVEE Ion Implanter of the Institute of Physics, Porto Alegre. The beam current density was lower than  $1 \mu\text{A}/\text{cm}^2$  in order to avoid excessive heating of the sample, and the implanted fluence was  $3 \times 10^{15}$  at/cm<sup>2</sup>. The Bi implantation energy was chosen such that the maximum of the Bi profile coincides with the interface of the Al/V system being the peak concentration around 1.2 at %.

The depth distributions were measured by the RBS technique using a 760-keV  $^4\text{He}^{++}$  beam. Particles scattered at 160° with respect to the beam direction were energy analyzed by a standard Si surface barrier detector. The energy resolution of the electronic detection system was 12 keV, which corresponds to 92 Å depth resolution in V. In some experiments two RBS energy spectra have been taken; one with normal  $\alpha$  incidence (0° geometry) and the second at an angle of 40° between the directions of the  $\alpha$  beam and the normal to the sample surface (40° geometry in Fig. 1).

The thermal annealings of the Al/V sample were performed at 200, 300, 400, 500, and 550 °C for 3 h at each temperature, at 580 and 610 °C for 2 h, and at 640 °C for 1 h; the upper temperature was chosen by taking into account the phase diagram of the Al-V system, since alloys are formed at higher temperatures. The pure V was annealed at 200, 400, 500, 600, and 700 °C 1 h each, covering the same temperature range as for the composed system. All the annealings were made in a vacuum better than  $10^{-6}$  Torr. Preliminary results in a similar system Al (500 Å)/V have been previously reported.<sup>1</sup>

## III. EXPERIMENTAL RESULTS

### A. Al/V system

The range profile of Bi in the as-implanted sample, displayed in Fig 1, barely shows a discontinuity at the interface. The discontinuity is more clearly seen after the measurement performed at the 40° geometry (see insert of Fig. 1) when the depth resolution is improved.

Annealings up to 500 °C did not bring any significant change to the implanted profile; in particular the discontinuity

<sup>a)</sup> On leave from Universidade Federal de São Carlos, SP, Brasil.

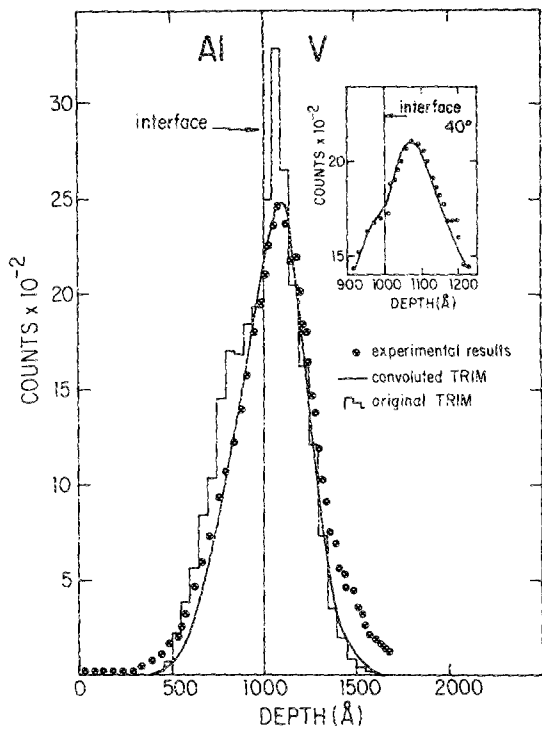


FIG. 1. Profile of 350-keV  $^{209}\text{Bi}^+$  implanted in the Al(1000 Å)/V bilayer structure. Full points: experimental RBS data; histogram: TRIM theoretical prediction; full line: convolution of the TRIM calculation with the detector resolution. The insert shows the profile at the interface region with an improved depth resolution (geometry of  $40^\circ$ ), and where the smooth curve is the convoluted TRIM calculation.

uity of the Bi profile at the interface did not change (see Fig. 2). At  $580^\circ\text{C}$  thermal diffusion of the implanted ions starts and is characterized by a slight decrease of the Bi concentration under the peak. Further annealings at  $610^\circ\text{C}$  and  $640^\circ\text{C}$  show a more pronounced diffusion process manifested by a diminution of the Bi concentration and broadening of the whole range profile. It is important to remark that after the annealing performed at  $640^\circ\text{C}$ , the shape of the diffused profile still resembles the implanted one, being only broader and smaller as a consequence of the thermal diffusion that has occurred (see Fig. 3).

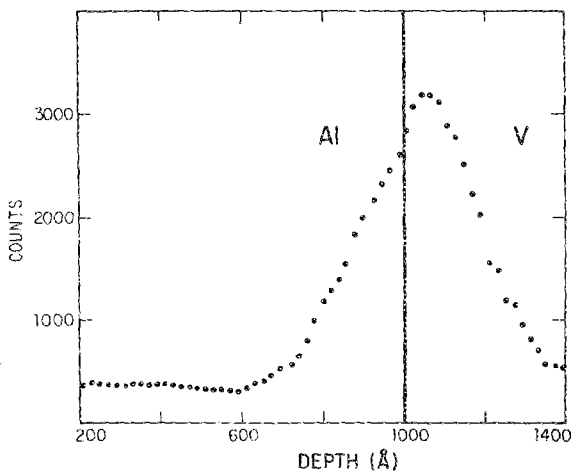


FIG. 2. Profile of 350-keV  $^{209}\text{Bi}^+$  implanted in the Al(1000 Å)/V system after annealing at  $550^\circ\text{C}$ .

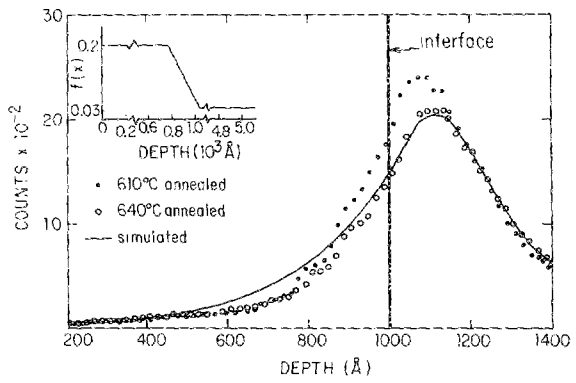


FIG. 3. Profile distributions of  $^{209}\text{Bi}$  implanted in the bilayer Al(1000 Å)/V after annealings at  $610^\circ\text{C}$  and  $640^\circ\text{C}$ . The smooth line represents the simulated distribution using the depth parameter  $g(x)$  with  $f(x)$  as shown in the insert.

### B. Pure V

The measured values of the implanted Bi range distribution in pure V are  $R_p = 330 \text{ Å}$  and  $\Delta R_p = 125 \text{ Å}$ . Annealings performed up to  $500^\circ\text{C}$  have not changed the implanted profile at all. A slight decrease in the Bi concentration is visible at  $600^\circ\text{C}$ , but noticeable regular diffusion only develops after the annealing at  $700^\circ\text{C}$  as is shown in Fig. 4, where the depth distributions after  $600^\circ\text{C}$  and  $700^\circ\text{C}$  annealings are displayed.

## IV. DISCUSSION

### A. As-implanted samples

One of the purposes of the present work is to compare the experimental Bi profile implanted in the Al/V system with very recent calculations, which make use of a new universal potential and an improved electronic stopping power.<sup>5,6</sup> These calculations have been performed using the latest version of the TRIM Monte-Carlo simulation code.

Figure 1 shows the experimental depth profile together with both the TRIM range distribution calculation and the convolution of the calculated distribution with the experimental depth resolution. Comparison between theory and

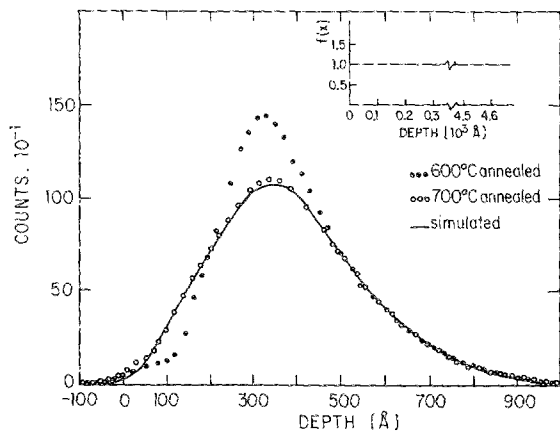


FIG. 4. Profile distributions of  $^{209}\text{Bi}$  implanted in pure V after annealings at  $600^\circ\text{C}$  and  $700^\circ\text{C}$ . The smooth line represents the simulated distribution using the depth parameter  $g(x)$  with  $f(x)$  as shown in the insert.

experiment shows a good agreement and the profile's structure at the Al/V interface is very well reproduced by the TRIM calculations.

The measured projected range  $R_p = 330 \text{ \AA}$  and projected range straggling  $\Delta R_p = 125 \text{ \AA}$  for 250 Bi implanted in pure V are also in good agreement with the TRIM calculated values,  $R_p = 310 \text{ \AA}$  and  $\Delta R_p = 130 \text{ \AA}$ .

### B. Thermal behavior of the implanted systems

It is not straightforward to carry out data evaluation of thermal annealing experiments performed after implantation into multilayer systems. This is basically due to two main reasons. First, the original profile is not a Gaussian distribution. Second, it is well known that the damage produced by the implantation does not always anneal out during or immediately after the implantation. Consequently, the implanted ions do not follow a regular diffusion, but a diffusion which is influenced by the defects produced by the irradiation and not annealed out. Therefore, it is very difficult to describe the experimental results by analytical methods, unless only the very general features of the experiment are going to be extracted.

In our work, the thermal diffusion after ion implantation into the bilayer system, is analyzed by using a numerical simulation method called "finite difference method." The mathematical background of this technique is found in Ref. 7 and some earlier applications are described in Refs. 8–10. With this method any input profile can be diffused independent of its shape, by introducing an appropriate depth-dependent diffusion parameter  $g(x) = g f(x)$ , where  $g$  is the diffusion parameter and  $f(x)$  is the depth functional dependence. This method is adequate for use in bilayer systems and/or in systems which due to irradiation effects follow enhanced or retarded diffusion, as it is described in Ref. 2. Using a computer program based on this technique, we were able to estimate the Bi diffusion coefficients in the V bulk of the Al/V bilayer system as well as in pure V. On the other hand Bi is essentially insoluble in Al (at least in the present temperature range), hence, no regular diffusion is expected to occur. The experimental results have confirmed this assumption and consequently no attempt has been made to determine the Bi diffusion coefficients in Al films.

To analyze the diffusion in the Al/V bilayer system we have introduced three different diffusion parameters. One for the Al film, a second for the V bulk, and a third one characterizing the interface region. This procedure is standard for the diffusion at any annealing temperature.

Figure 3 shows a typical example of the above procedure. The full points represent the initial depth profile, which in the present case is the one obtained after 610 °C annealing. The open points show the final ion distribution after annealing at 640 °C. The insert of Fig. 3 displays the depth-dependent diffusion parameter used by the program in order to reproduce the final ion distribution. From the surface up to 780 Å,  $f(x)$  is equal to 0.2; then, there is a variable diffusion parameter from 780 Å up to 1030 Å, characterizing the interface region; and finally a third constant diffusion parameter  $f(x) = 0.03$  corresponding to the V bulk.

Starting from the initial range profile and applying the  $f(x)$  parameter, the program, after several iterations, provides the depth profile shown in the figure as a full line. The agreement between the experimental result and the simulated one is quite satisfactory for the V and interface regions, and as expected, rather poor for the Al film. The extracted diffusion parameter for Bi in the V bulk is  $D_{\text{Bi-V}} = 7.5 \times 10^{-17} \text{ cm}^2/\text{s}$ .

Similar depth-dependent diffusion parameters have been used in order to reproduce the spectra at other annealing temperatures. The obtained diffusion coefficients of Bi in the V bulk are shown in Table I. Despite the fact that there are only three experimental points, we can estimate the diffusion coefficient from the Arrhenius plot as shown in Fig. 5. The result is:  $D = 5 \times 10^{-5} \exp(-2.2 \text{ eV}/kT) \text{ cm}^2/\text{s}$ .

As was mentioned in Sec. III B, up to 500 °C there is no observable Bi diffusion in the pure V foil. A slight diffusion starts at 600 °C characterized by a diffusion coefficient  $D < 10^{-17} \text{ cm}^2/\text{s}$ . A noticeable diffusion only begins after annealing at 700 °C. The open circles of Fig. 4 show the Bi distribution after annealing at 700 °C and the full line simulates a regular diffusion (see insert). The agreement is quite good and the extracted diffusion coefficient  $D = 1.35 \times 10^{-16} \text{ cm}^2/\text{s}$  is quoted in Table I.

The analysis of the Bi diffusion in both systems (Al/V and pure V) was performed assuming nonreflective surfaces. That is, the Bi ions leave the system whenever they reach the surface. The agreement between the experimental and calculated results, in particular for the pure V foil confirms the assumption, and this is the reason why the area of the initial and final depth profile in Fig. 4 is not conserved. Finally, it should be pointed out that there is no available data concerning Bi solubility in V. However, the fact that regular diffusion has been observed is a hint that the Bi implanted concentration is, for the studied temperatures, below the solubility limit.

### V. CONCLUSIONS

One of the main purposes of the present work is to compare the experimental range profile of the Bi ions, implanted in the Al/V bilayer structure, with the predictions of the TRIM program. The calculations reproduce the Bi concentration in the whole range profile and, in particular, at the interface region. This kind of agreement, also observed for

TABLE I. Diffusion data extracted from present experiment and from Ref. 15.  $D_{\text{Bi-V}}$  and  $D_{\text{Al-V}}$  are, respectively, the diffusion coefficients of Bi in V and Al in V.

$T$ °C	Al/V bilayer $D_{\text{Bi-V}}$ $\text{cm}^2/\text{s}$	Pure V	
		$D_{\text{Bi-V}}$ $\text{cm}^2/\text{s}$	$D_{\text{Al-V}}^a$ $\text{cm}^2/\text{s}$
580	$1.15 \times 10^{-17}$		
600	...	$1 \times 10^{-17}$	$2 \pm 1.4 \times 10^{-17}$
610	$2.9 \times 10^{-17}$		
640	$7.5 \times 10^{-17}$		
700	...	$1.35 \times 10^{-16}$	$3 \pm 0.9 \times 10^{-16}$

<sup>a</sup> Reference 15.

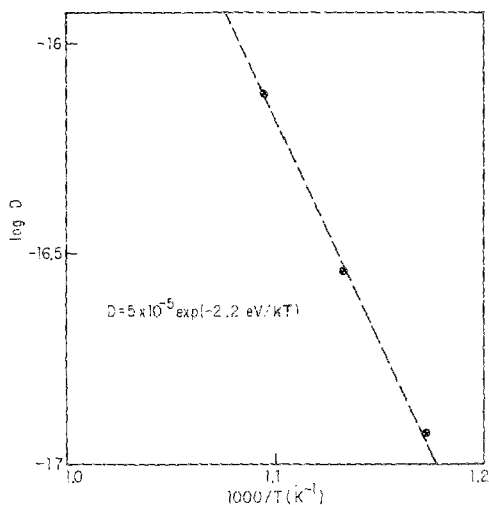


FIG. 5. Arrhenius diagram for the  $^{209}\text{Bi}$  diffusion in the V substrate of the Al/V bilayer system.

Al/Ti (Ref. 1) and Al/KCl (Ref. 2) systems gives further support to the theoretical assumptions inserted in the TRIM program adapted for multilayer systems.

Concerning the thermal behavior of the implanted Bi ions, several features can be pointed out. Here, as in the Al/KCl system, we also have to include a depth-dependent diffusion constant for a relatively broad region around the interface in order to account for possible structural near-interface imperfections.

The fact that the basic structure of the Bi profile (including the discontinuity at the interface) is conserved for temperatures up to 550 °C is a strong evidence that in the Al film as well as at the interface region, we are in the presence of a retarded diffusion. This assumption is supported by results of a previous experiment where Bi implanted into pure Al foil shows a rapid diffusion and hence completely flat distribution after annealing at 400 °C (see Fig. 4 of Ref. 1). This means that the evaporated Al layer, in contrast to bulk Al, proves to be a trap-enriched zone for the implanted Bi ions. This behavior was already observed in the Al/Ti (Ref. 1) and Al/KCl (Ref. 2) systems.

The Bi ions only start a regular diffusion in the V substrate of the compound system at 580 °C. Despite the few experimental points we can estimate the diffusion coefficients as  $D = 5 \times 10^{-5} \exp(-2.2 \text{ eV}/kT) \text{ cm}^2/\text{s}$ . There are no previous available data of Bi diffusion into V in order to compare with the present results. On the other hand several works have been performed concerning vanadium self-diffusion,<sup>11</sup> Fe,<sup>12</sup> Co,<sup>13</sup> and Ta (Ref. 14) diffusion in vanadium. All these studies have been done in a temperature range much higher than the present (typically 1000–1800 °C). The obtained  $D_0$  coefficients vary from  $9.45 \times 10^{-3}$  to  $4.24 \text{ cm}^2/\text{s}$ , and the activation energy is typically of the order of 3 eV, a value characteristic of a normal diffusion behavior through a single-vacancy mechanism. More recently Lappalainen<sup>15</sup> has studied the Al diffusion in V in a lower temperature range (600–1000 °C). The least-squares fit to their experimental data gives

$$D = (3 \pm_{2.5}^{10}) \times 10^{-4} \exp(-2.4 \text{ eV}/kT) \text{ cm}^2/\text{s}.$$

Our results agree well with the data of Lappalainen<sup>15</sup> and are also in reasonable agreement with other measurements performed in V: V self-diffusion and diffusion of Fe, Co, and Ta in V bulk. In addition, as displayed in Table I, our measured diffusion constants for Bi in pure V are consistent with the results of Ref. 15 for Al in V. All these facts indicate that the diffusion mechanism of Bi in pure V, in the V substrate of the Al/V system and of Al in pure V, is basically the same.

The interpretation of our diffusion results are limited by the low-temperature range and also by the few experimental points. Taking into account these limitations, the present results are consistent with a vacancy diffusion mechanism. Alternatively, we cannot completely exclude the occurrence of diffusion through short-circuit paths mechanism, which could be responsible for the somewhat low activation energy value  $E_a = 2.2 \text{ eV}$  obtained in this work, as compared with 3 eV (see Ref. 13).

In conclusion, the diffusion results of this work show that Bi mobility is largely hindered in the Al film of the Al/V system, behavior which was already observed in previous works.<sup>1,2</sup> At present we do not have a plausible explanation for this behavior. In principle, it could be attributed to non-annealed strains produced in the Al film when it is evaporated on the V bulk. On the other hand Bi diffuses regularly in the V bulk of the Al/V system with the same mechanism as in pure V.

#### ACKNOWLEDGMENTS

The authors are grateful to Dr. M. P. Macht and Dr. V. Naundorf of the HMI for the very stimulating discussions. This work was supported in part by CNPq, FINEP, and CAPES.

- <sup>1</sup>C. A. Olivieri, M. Behar, P. F. F. Fichtner, F. C. Zawislak, D. Fink, and J. P. Biersack, *J. Appl. Phys.* **58**, 659 (1985); *Nucl. Instrum. Methods B* **15**, 78 (1986).
- <sup>2</sup>M. Behar, J. P. Biersack, P. F. F. Fichtner, D. Fink, C. A. Olivieri, and F. C. Zawislak, *Nucl. Instrum. Methods B* **14**, 173 (1986).
- <sup>3</sup>J. P. Biersack and L. G. Haggmark, *Nucl. Instrum. Methods* **174**, 257 (1980).
- <sup>4</sup>L. Pelikán, V. Rybka, P. Krejci, V. Hnatowicz, and J. Kvítek, *Phys. Status Solidi (A)* **72**, 369 (1982).
- <sup>5</sup>J. P. Biersack and J. F. Ziegler, in *Springer Series in Electrophysics, Vol. 10: Ion Implantation Techniques*, edited by H. Ryssel and H. Glawischnig (Springer, Berlin, 1982), pp. 122–156.
- <sup>6</sup>J. F. Ziegler, J. P. Biersack, and U. Littmark, *Proceedings of the U.S.–Japan Seminar on Charged Particle Penetration Phenomena*, ORNL, Report CONF-820131 (1982), p. 88.
- <sup>7</sup>G. D. Smith, *Numerical Solution of Partial Differential Equations: Finite Difference Methods*, 2nd ed. (Claventon, Oxford, 1978).
- <sup>8</sup>J. P. Biersack and D. Fink, in *Ion Implantation in Semiconductors*, edited by S. Namba (Plenum, New York, 1974), pp. 211–218.
- <sup>9</sup>J. P. Biersack and D. Fink, in *Proceedings of the 8th Symposium on Fusion Technology*, Noordwijkerhout, June 17–21, 1974 (Commission of the European Communities, Luxembourg, 1974), pp. 907–913 (Conf. EUR 5182 e).
- <sup>10</sup>T. Kie, Ph.D. thesis (Free University of Berlin, 1985).
- <sup>11</sup>J. Pelleg, *Philos. Mag.* **29**, 383 (1974).
- <sup>12</sup>D. Ablitzer, J. P. Haussler, K. V. Sathyaraj, and A. Vignes, *Philos. Mag.* **A 44**, 589 (1981).
- <sup>13</sup>J. Pelleg, *Philos. Mag.* **32**, 593 (1975).
- <sup>14</sup>J. Pelleg and M. Herman, *Philos. Mag.* **35**, 349 (1977).
- <sup>15</sup>R. Lappalainen, *Nucl. Instrum. Methods B* **7/8**, 44 (1985).