



## Perturbed angular correlation studies of the MAX phases $\text{Ti}_2\text{AlN}$ and $\text{Cr}_2\text{GeC}$ using ion implanted $^{111}\text{In}$ as probe nuclei

Daniel Jürgens<sup>a,\*</sup>, Michael Uhrmacher<sup>a</sup>, Hans Hofsäss<sup>a</sup>, Jose Mestnik-Filho<sup>b</sup>, Michel W. Barsoum<sup>c</sup>

<sup>a</sup> II. Physikalisches Institut, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany

<sup>b</sup> Instituto de Pesquisas Energéticas e Nucleares, CP 11049, Pinheiros, 05422-970 São Paulo, SP, Brazil

<sup>c</sup> Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA

### ARTICLE INFO

#### Article history:

Available online 26 February 2010

#### Keywords:

MAX phases

Radioactive ion implantation

Hyperfine interactions

Perturbed angular correlation (PAC)

### ABSTRACT

PAC measurements were done for the first time on the 211-MAX phases  $\text{Ti}_2\text{AlN}$  and  $\text{Cr}_2\text{GeC}$  which do not have indium as a constituent material. Radioactive  $^{111}\text{In}^+$  ions were implanted at 400 keV into the MAX bulk-samples. The radiation damage was annealed under vacuum up to temperatures of 1373 K. During each heating cycle the samples were sealed in new quartz tubes, as a loss of the  $^{111}\text{In}$  probes out of the samples was observed at high temperatures. Both MAX phases showed EFGs similar to the ones observed in indium containing MAX phases. In all cases they are attributed to probes residing on the A-site of the 211-structure. After high and long annealing temperatures an additional fraction of probes is observed in  $\text{Cr}_2\text{GeC}$  with a different EFG. The corresponding site may be the M-site of the 211-structure, or a site in  $\text{Cr}_2\text{C}$ . The comparison of the X-ray diffraction spectra, taken before the implantation and after the end of the PAC measurements, showed that  $\text{Cr}_2\text{GeC}$  partly disintegrates to  $\text{Cr}_2\text{C}$ .

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

The MAX phases are nanolaminated layered, hexagonal ternary carbides and nitrides with the general formula  $\text{M}_{n+1}\text{AX}_n$  (MAX). Here  $n$  goes from one to three, M is an early transition metal, A is an element mostly of the IIIB and IVB groups, formally called A-groups, and X is either C and/or N. The compounds belong to space group  $\text{D}_{6h}^4$ ,  $\text{P6}_3/\text{mmc}$  with two formula units per unit cell. Up to now roughly 60 compounds are known to exist. The vast majority of them have the  $\text{M}_2\text{AX}$  structure, henceforth referred as the 211-phases [1,2].

These phases combine some of the best attributes of metals and ceramics. Like metals, they are electrically and thermally conductive, easily machinable, plastic at high temperatures and highly damage tolerant. Like ceramics, they are elastically stiff, lightweight, oxidation and thermal shock resistant and maintain their strengths up to high temperatures [1,2]. The origin of this special set of properties can be found in its microstructure – influenced by kink band formation and microyielding of the nanolaminated configuration [3–5]. Electrical and mechanical characteristics of several phases have been studied extensively in the last few years, but mostly with macroscopic tools [6–8]. To obtain insight on the atomic scale, X-ray diffraction and transmission electron microscopy are routinely used.

A less common technique is the perturbed angular correlation method (PAC). Radioactive isotopes decaying by a  $\gamma$ - $\gamma$  cascade are utilized as probe nuclei, sensing their local surrounding via hyperfine interactions. All changes in the direct neighborhood of the probe atom (missing or trapped atoms, dislocations, ...) result in different electric or magnetic hyperfine fields. Ion implantation is a successful method to insert these “spies” in materials. In the present study the standard PAC isotope  $^{111}\text{In}$  was used which decays by electron capture to  $^{111}\text{Cd}$  with a half life of 2.83 days. Therefore, PAC measurements can be performed during 2–3 weeks, until most of the probes have decayed.

An important point for any data interpretation in PAC spectroscopy is knowing which lattice site the probe atoms occupy. For some MAX phases this question can easily be answered by choosing the compounds which have indium as a constituent. Owing to that consideration, previous experiments were performed for the key-compounds  $\text{Ti}_2\text{InC}$  and  $\text{Zr}_2\text{InC}$  [10] since the A-element is chemically identical to the  $^{111}\text{In}$  atoms. One expects that the probes occupy the In-site or more generally the A-site. It has been shown (for example for the delafossites [9]) that within a family of different compounds with the same structure one PAC-probe senses similar EFGs (in strength and symmetry). Simply speaking, one gets a “fingerprint” of a certain lattice site. We found in [10] that these phases show, after long annealings at high temperatures, axially symmetric EFGs with quadrupole coupling constants of  $\nu_{Q1} = 291(1)$  MHz for  $\text{Ti}_2\text{InC}$  and  $\nu_{Q1} = 345(2)$  MHz for  $\text{Zr}_2\text{InC}$ .

\* Corresponding author. Tel.: +49 551 397 628; fax: +49 551 394 493.  
E-mail address: [djuerge@gwdg.de](mailto:djuerge@gwdg.de) (D. Jürgens).

Using  $^{111}\text{In}$  in other 211-phases which do not contain indium as a constituent, one expects an EFG in the same range of about 300 MHz assuming  $^{111}\text{In}$  atoms at A-sites. The purpose of this work is to characterize the A-site EFG parameters for  $^{111}\text{In}$  incorporated in the compounds  $\text{Ti}_2\text{AlN}$  and  $\text{Cr}_2\text{GeC}$  and to study the annealing behavior after implantation of In probe atoms.

## 2. Experimental details

Polycrystalline samples of  $\text{Ti}_2\text{AlN}$  and  $\text{Cr}_2\text{GeC}$  were fabricated as bulk material. Their synthesis rely on the principle of hot isostatic pressing (HIP) whereas the optimal process parameters for different compounds vary among each other. The starting point is pure elemental powders mixed in the right stoichiometric ratio via dry ball milling and cold pressed afterwards. The resulting pellets were sealed under vacuum in borosilicate ampullae and placed in a HIP working with an applied pressure in the range of 40–100 MPa at temperatures from 800 K to a maximum of 1700 K for several hours. Further details of the phase fabrication are described elsewhere [11,12]. The HIPed samples were cut into 10–15 mm<sup>2</sup> slices of about 1 mm thickness using spark erosion.

Into each sample approximately  $10^{12}$   $^{111}\text{In}^+$  ions were implanted at 400 keV using the Göttingen Cockcroft–Walton type implanter IONAS [13]. The radioactive material was obtained from Perkin Elmer as carrier free  $^{111}\text{InCl}_3$  solution. Microlitre droplets were placed on a hollowed tip of a support rod and dried by an infrared heating lamp. After covering the tip with a little tube it was inserted in the SO55 ion source of IONAS. The  $^{111}\text{In}$  transmission from source to target is typically 20%, in the best cases 25% [14]. For  $\text{Ti}_2\text{AlN}$  the ion range calculated with the code stopping and range of ions in matter (SRIM) [15] is about 113 nm having a straggling width of 37 nm. In the case of  $\text{Cr}_2\text{GeC}$ , it is 81 nm with 30 nm distribution. The induced radiation damage caused by the implantation was annealed at different temperatures and duration steps in vacuum. Afterwards PAC measurements were performed at room temperature using a standard setup with four NaI(Tl)-detectors in 90° geometry which allows a simultaneous recording of eight 90° and four 180° coincidence spectra. From these twelve spectra the experimental perturbation  $R(t)$  can be calculated. Data analysis details are described in Ref. [16].

All annealings were performed in evacuated and sealed quartz ampullae to prevent oxidation. In the course of these procedures we observed in  $\text{Cr}_2\text{GeC}$  a strong correlation between the increase of the annealing temperature and the loss of radioactive  $^{111}\text{In}$  from the specimens. Above 1000 K more than 25% of the still present  $^{111}\text{In}$  probes were lost from the samples, reaching a maximum value of 45–65% at 1273 K depending on the annealing duration. Previous studies of indium containing MAX phases have shown that the loss occurred by the precipitation of excessive indium [10].

In the present case, grayish discolorations within the quartz tubes were observed. We suppose that these discolorations resulted from non-reacted germanium or chromium which might coincide with the loss of  $^{111}\text{In}$ . Additionally the indium loss in  $\text{Cr}_2\text{GeC}$  might be favored by the porous surface character (see Fig. 1). The large inner surface would enhance the possibility for  $^{111}\text{In}$  to diffuse out, encouraged by the low melting point of indium ( $T_{\text{melt}} = 430$  K) compared to the applied annealing temperatures.

To reduce the loss of  $^{111}\text{In}$  during tempering a small piece of inactive  $^{115}\text{In}$  was inserted in one ampulla to create an indium-backpressure. However, after annealing for 2 h at 1273 K more than 90% of the current activity was found in the attached indium piece. In addition a large amount of  $^{115}\text{In}$  diffused into the sample. This can be concluded, as 80% of the still present probes moved within the sample into the newly present In-metal, proved by the well established EFG of  $\nu_Q = 17.3$  MHz [17].

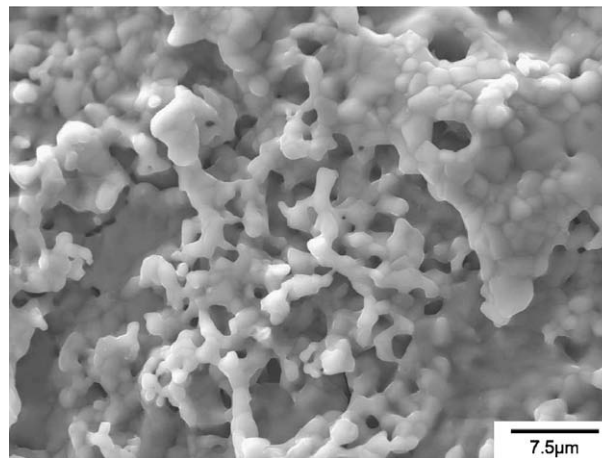


Fig. 1. SEM picture of a  $\text{Cr}_2\text{GeC}$  sample after finishing PAC measurements. The features seen here are most probably due to the spark erosion.

To avoid a PAC signal from probes present on the inner surface of the ampullae, the quartz tubes were removed directly after each annealing step. The following PAC measurements were performed at RT in air with the samples enclosed in plexiglas trays.

## 3. Results and discussion

### 3.1. The 211-system $\text{Ti}_2\text{AlN}$

Based on previous PAC studies of the indium containing MAX phases,  $\text{Ti}_2\text{InC}$  and  $\text{Zr}_2\text{InC}$  [10], the indium-free compound  $\text{Ti}_2\text{AlN}$  was chosen to look for a similar EFG value according to the “fingerprint approach”. Due to the chemical relationship of aluminium and indium – both are members of the group IIIA in the periodic table – it is reasonable to assume that the implanted  $^{111}\text{In}$  ions occupy the Al-site. Based on the known vacuum annealing parameters of the In-MAX phases an annealing temperature of 1073 K was applied for 1 h. After this treatment all probes sensed the same local surrounding. The PAC spectra showed a sharp axially symmetric EFG fitted with the quadrupole coupling constant  $\nu_{Q1} = 259(2)$  MHz and a distribution width  $\delta_{Q1} = 1$ –2% (see Fig. 2). The strength of the EFG in  $\text{Ti}_2\text{AlN}$  is comparable to the one found in  $\text{Ti}_2\text{InC}$  in which the probes are presumably located on the In-sites. This result confirms that the  $^{111}\text{In}$  probes were integrated on the same lattice sites creating an EFG in the same range of  $\nu_Q$  as in  $\text{Ti}_2\text{InC}$ .

Besides the determination of the probes’ lattice location we note that the shape of the perturbation function  $R(t)$  deviates from the one of random polycrystalline samples which show pure electric quadrupole interaction. For the latter the ratio of the transition frequency intensities in Fourier space takes  $\omega_1 : \omega_2 : \omega_3 = 3 : 2 : 1$  according to Ref. [16]. In  $\text{Ti}_2\text{AlN}$  we observed a ratio of 7:2:1 in horizontal sample alignment which indicates a texture within the

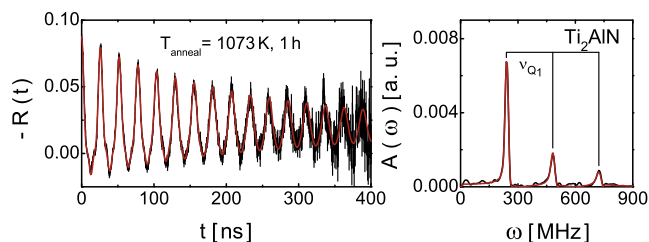
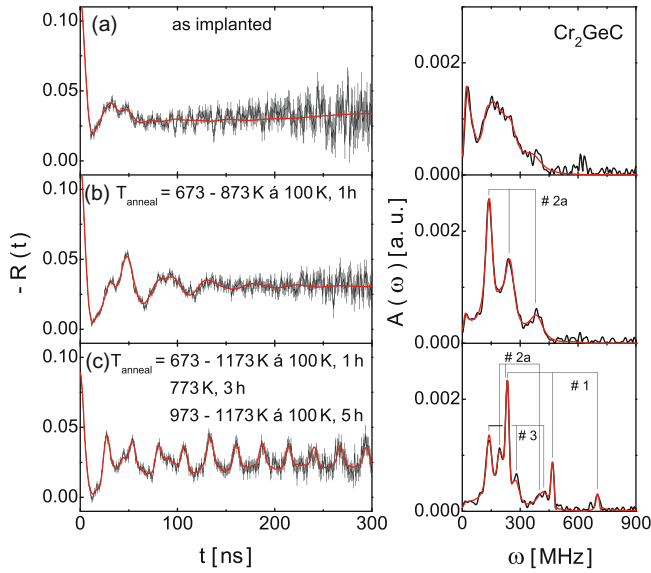


Fig. 2. PAC spectrum and its Fourier transformation of annealed  $\text{Ti}_2\text{AlN}$ .



**Fig. 3.** PAC spectra with Fourier transforms of  $^{111}\text{In}$  in  $\text{Cr}_2\text{GeC}$  for different annealing steps measured in air. Labeling according to Table 1.

main plane of the sample, most likely caused by the machining operation.

### 3.2. The 211-system $\text{Cr}_2\text{GeC}$

Up to now all MAX phases studied with PAC spectroscopy had the following in common: the elements of the M-layers as well as the ones of the A-layers belonged to the same groups, e.g. Ti and Zr are from group IVB, whereas Al and In are from group IIIA [1]. The compound  $\text{Cr}_2\text{GeC}$  is of special interest since both constituents – Cr and Ge – take other positions in the periodic table. Therefore the numbers of valence electrons vary which might have an influence on the strength of the EFG.

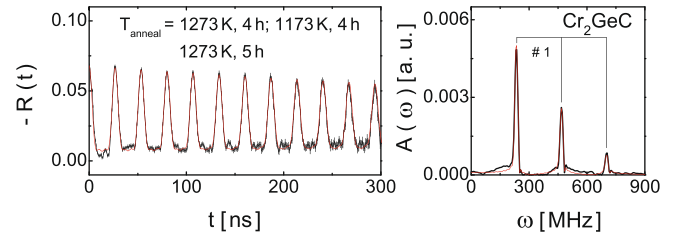
Perturbed angular correlation spectra of  $\text{Cr}_2\text{GeC}$  were recorded after several annealings (see Fig. 3). First, samples were heated in 100 K steps in the range of 673 K up to 1173 K for 1 h in evacuated quartz ampullae which were cracked open after each annealing and before a PAC measurement. The resulting experimental  $R(t)$  functions were fitted assuming a small fraction of  $f_1 = 2\text{--}15\%$  with a low-frequency coupling constant of  $\nu_{Q_1} = 15\text{--}30$  MHz and a dominant contribution,  $f_2 = 85\text{--}98\%$ , with  $\nu_{Q_2} = 130\text{--}135$  MHz. But the latter features a distribution width of  $\delta_{Q_2} = 12\text{--}14\%$  and an asymmetry parameter  $\eta$  of about 0.35–0.40 (see Fig. 3(b)).

The attempt to observe a clear PAC signal like obtained in other 211-phases required now a second annealing cycle in which the heating period was raised to 5 h, starting at 873 K and ending at 1273 K. Already after  $T_{\text{anneal}} = 973$  K the hyperfine parameters reached nearly constant values, using a fit with three different fractions listed in Table 1. One of these  $R(t)$  curves is illustrated in Fig. 3(c).

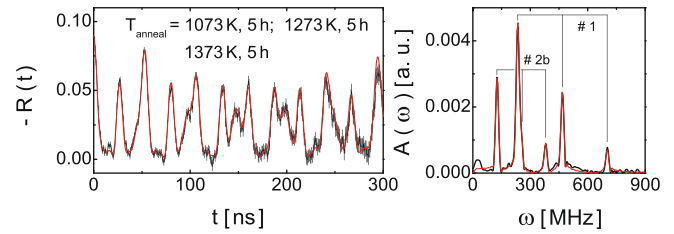
**Table 1**

Range of hyperfine parameters for  $\text{Cr}_2\text{GeC}$  measured at room temperature after each 5 h annealing. The fraction signifies the percentage of the probes sensing the same surrounding,  $\nu_Q$  is the quadrupole coupling constant describing the strength of the corresponding EFG,  $\delta_Q$  features its distribution width and  $\eta$  is the asymmetry parameter of the EFG.

Site	Fraction (%)	$\nu_Q$ (MHz)	$\delta_Q$ (%)	$\eta$
# 1	25–33	249–250	0–1	0.00
# 2a	32–35	132–135	5–8	0.76–0.80
# 2b	35–39	134–135	0–1	0.00
# 3	37–44	146–149	8–13	0.00



**Fig. 4.** PAC spectrum and its Fourier transform of  $^{111}\text{In}$  in  $\text{Cr}_2\text{GeC}$ . Sample stayed for quoted annealing procedure in the same quartz ampulla which was removed for the shown measurement. Labeling according to Table 1.



**Fig. 5.** Recorded PAC spectrum and its Fourier transform of  $^{111}\text{In}$  in  $\text{Cr}_2\text{GeC}$  while trying to reproduce the previous result of Fig. 4(b). The sample has been heated before implantation at 1273 K for 5 h.

As mentioned in Section 2 the removal of the ampullae after high temperature annealings is of great importance as can be seen in Fig. 4, where nearly all probe atoms sense the same surrounding which manifests itself in a sharp axially symmetric EFG, fitted by a quadrupole coupling constant of  $\nu_{Q_1} = 249(1)$  MHz and a small distribution width of  $\delta_{Q_1} = 0.4(1)\%$ .

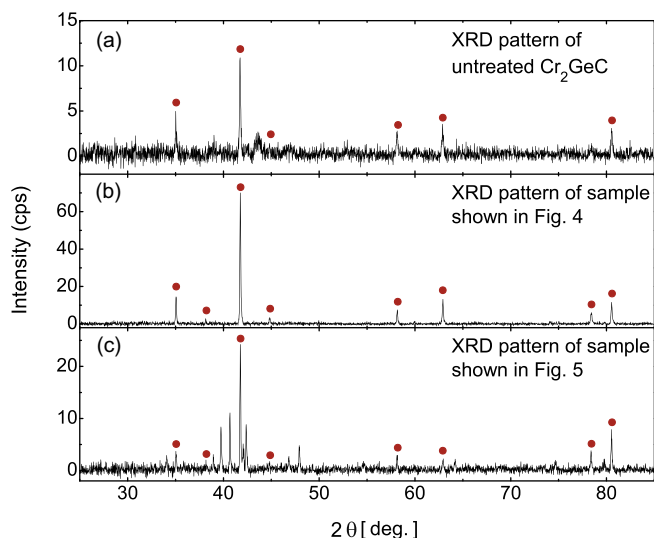
The strength of the observed EFG is very close to the one which was found in  $\text{Ti}_2\text{AlN}$  and  $\text{Ti}_2\text{InC}$ . Due to this relation and previous considerations it can be assumed that the probes occupy the germanium site or more generally the A-site in  $\text{Cr}_2\text{GeC}$ .

Further experiments were performed to reproduce this result and to look for a recipe to obtain such spectra by varying annealing temperatures and durations. By choosing long heating cycles at high temperatures even before implantation, not only the known A-site EFG appeared but also a fraction of approximately 40% occurred featuring a new, axially symmetric EFG with  $\nu_{Q_{2b}} = 135(1)$  MHz (see Fig. 5).

X-ray diffraction studies have shown a partial phase dissociation, whereas some binary compounds were formed (see Section 3.3). A site in a dissociation product would be a possible explanation. Another one is to assume that probes have replaced the chromium atoms, that means they occupy the M-sites of the 211-phase. As a result the new EFG would be the counterpart of the A-site EFG. One can prove such assumptions by performing FP-LAPW calculations which are based on density functional theory. Here one has to place the probe on both chromium and germanium sites and compare the theoretical results with the experimental ones. Such simulations are in progress.

### 3.3. XRD measurements

In addition to PAC measurements X-ray diffraction spectra were recorded in  $\theta - 2\theta$  geometry to determine the phase composition of  $\text{Ti}_2\text{AlN}$  and  $\text{Cr}_2\text{GeC}$  slices before the implantation and later after all PAC measurements. Due to discolorations of some of the heated quartz tubes XRD was used to check for possible phase transitions or dissociations. In the case of  $\text{Ti}_2\text{AlN}$  the applied annealings induced only a small decrease of the present  $\text{Ti}_2\text{Al}$  and  $\alpha - \text{TiN}_{0.3}$



**Fig. 6.** X-ray diffraction patterns of  $\text{Cr}_2\text{GeC}$  samples after different heat treatments. (a) Starting material, (b) scan of sample which has shown only one EFG (see Fig. 4) and (c) scan of sample with two axially symmetric EFGs from Fig. 5.  $\text{Cr}_2\text{GeC}$  reflections are labeled with dots.

reflection intensities. Pieces of untreated  $\text{Cr}_2\text{GeC}$  included already small amounts of binary phases like  $\text{Cr}_{11}\text{Ge}_8$  and  $\text{Cr}_7\text{C}_3$ . Heating these samples caused different results which are shown in Fig. 6. In part (b) the intensities of all MAX reflections have increased by a factor greater than 3 which implies that the phase synthesis was not totally completed and the additional annealing improved the MAX phase quality (see Fig. 6(b)). The opposite case, that a partial decomposition took place is illustrated in Fig. 6(c) where  $\text{Cr}_2\text{C}$  was generated among others. The new EFG of  $\nu_{Q_{2b}} = 135$  MHz which was observed could possibly originate from probes in the  $\text{Cr}_2\text{C}$  phase or as discussed above from the M-site in the MAX phase. A systematic PAC investigation of the decomposition products has not taken place yet but is planned for the near future.

#### 4. Conclusion

In  $\text{Ti}_2\text{AlN}$  we observed an axially symmetric EFG with  $\nu_{Q_1} = 259(2)$  MHz in agreement with the expectations [10] for

the EFG strength for  $^{111}\text{In}$  atoms on the A-site. The phase  $\text{Cr}_2\text{GeC}$  showed a similar EFG of  $\nu_{Q_1} = 249$  MHz confirming the “fingerprint approach” for the A-site. After annealing to 1373 K a second In-site is observed which may be either due to the  $^{111}\text{In}$  residing on the M-site or a site in  $\text{Cr}_2\text{C}$ . To achieve a high fraction of  $^{111}\text{In}$  on the A-site in  $\text{Cr}_2\text{GeC}$ , high annealing temperatures and long annealing times are required which also causes a significant loss of In-probes.

#### Acknowledgements

We like to thank Detlef Purschke for successfully performed  $^{111}\text{In}$  implantations, Hans-Gregor Gehrke for providing SEM images as well as Volker Ebrecht for technical help. A part of this work was financially supported by the German Research Foundation (DFG) under Contract No. HO 1125/19-1 and by the National Science Foundation (DMR 0503711).

#### References

- [1] M.W. Barsoum, T. El-Raghy, *Am. Sci.* 89 (2001) 334.
- [2] M.W. Barsoum, *Prog. Solid State Chem.* 28 (2000) 201.
- [3] M.W. Barsoum, L. Farber, T. El-Raghy, *Metall. Mater. Trans. A* 30 (1999) 1727.
- [4] M.W. Barsoum, T. Zhen, A.G. Zhou, S. Basu, S.R. Kalidindi, *Phys. Rev. B* 71 (2005) 134101.
- [5] A.G. Zhou, S. Basu, M.W. Barsoum, *Acta Mater.* 56 (2008) 60.
- [6] M.W. Barsoum, H.-I. Yoo, I.K. Polushina, V.Yu. Rud, Yu.V. Rud, T. El-Raghy, *Phys. Rev. B* 62 (2000) 10194.
- [7] T. El-Raghy, S. Chakraborty, M.W. Barsoum, *J. Eur. Ceram. Soc.* 20 (2000) 2619.
- [8] M.W. Barsoum, J. Golczewski, H.J. Seifert, F. Aldinger, *J. Alloy Compd.* 340 (2002) 173.
- [9] R.N. Attili, R.N. Saxena, A.W. Carbonari, J. Mestnik Filho, M. Uhrmacher, K.P. Lieb, *Phys. Rev. B* 58 (1998) 2563.
- [10] D. Jürgens, M. Uhrmacher, H. Hofsäuss, J. Röder, P. Wodniecki, A. Kulinska, M.W. Barsoum, *Hyperfine Interact.* 178 (2007) 23.
- [11] M.K. Drulis, H. Drulis, A.E. Hackemer, A. Ganguly, T. El-Raghy, M.W. Barsoum, *J. Alloy Compd.* 433 (2007) 59.
- [12] S. Gupta, D. Filimonov, V. Zaitsev, T. Palanisamy, M.W. Barsoum, *Wear* 264 (2007) 270.
- [13] M. Uhrmacher, H. Hofsäuss, *Nucl. Instrum. Meth. B* 240 (2005) 48.
- [14] M. Uhrmacher, M. Neubauer, W. Bolse, L. Ziegler, K.P. Lieb, *Nucl. Instrum. Meth. B* 139 (1998) 306.
- [15] J.F. Ziegler, M.D. Ziegler, J. Biersack, SRIM version 2008.03. <[www.srim2008.org](http://www.srim2008.org)>.
- [16] L. Aldon, M. Uhrmacher, C. Branci, L. Ziegler, J. Roth, P. Schaaf, H. Metzner, J. Olivier-Fourcade, J.C. Jumas, *Phys. Rev. B* 58 (1998) 11303.
- [17] H. Haas, D.A. Shirley, *J. Chem. Phys.* 58 (1973) 3339.