

## Investigation of Grain Growth and Stabilisation of Nanocrystalline Ni

H. Wolf<sup>1</sup>, Z. Guan<sup>1</sup>, H. Natter<sup>2</sup>, R. Hempelmann<sup>2</sup>, and Th. Wichert<sup>1</sup>

<sup>1</sup> Technische Physik, Universität des Saarlandes, D-66041 Saarbrücken, Germany

<sup>2</sup> Physikalische Chemie, Universität des Saarlandes, D-66041 Saarbrücken, Germany

**Keywords:** pulse-reverse-technique, thermal stabilisation, diffusion, moving grain boundaries

### Abstract

Nanocrystalline Ni produced by pulsed electro deposition (PED) was investigated by perturbed  $\gamma$ -angular correlation spectroscopy (PAC) using radioactive  $^{111}\text{In}$ . The stabilisation of the Ni grains by oxygen against growth during thermal treatment was investigated using different electrode materials or a modified PED process. In Ni samples not intentionally doped with oxygen, the conversion from nano- to polycrystalline Ni was observed to occur up to 1070 K.

### Introduction

Nanocrystalline materials are of general interest for many technological applications. The production of nanocrystalline materials by pulsed electro deposition (PED) offers some advantages compared to many other techniques since pure material is obtained at a high production rate [1,2,3]. The density of the deposited material reaches that of polycrystalline material making a subsequent compaction procedure unnecessary. Nanocrystalline Ni has been investigated with respect to a fundamental understanding of ferromagnetism in nanocrystals [4,5] as well as with respect to possible industrial applications [6]. However, nanocrystalline Ni is not stable against thermal treatment for temperatures above 550 K and, therefore, potential technological applications of this material are restricted. In order to overcome this problem attempts were performed to stabilise the nanocrystallites by the introduction of impurity atoms, like oxygen, into the grain boundaries [7].

The diffusion of impurity atoms into nanocrystalline materials is strongly affected by the high density of grain boundaries. The incorporation of  $^{111}\text{In}$ -atoms *ex-situ* by diffusion into initially nanocrystalline Ni was investigated in dependence of the temperature of pre-annealing treatment. The increase of the size of the nanocrystalline grains during annealing, which is accompanied by the reduction of the density of grain boundaries is studied via the diffusion behaviour of In atoms. The grain size is expected to be typical for the respective annealing temperature and annealing time.

### Experimental details

The PED process was performed as described by Natter et al. [3]. The composition of the electrolyte and the parameters used for the deposition of Ni are listed in Table 1. The particle size of nanocrystalline Ni particles prepared by PED is typically in the range of 15 nm to 50 nm. For the PAC investigations, the samples were doped with  $^{111}\text{In}$  either *in-situ* by adding  $^{111}\text{InCl}_3$  to the electrolyte or *ex-situ* by thermal diffusion. Natter et al. reported the stabilisation of nanocrystalline Ni against grain growth at enhanced temperatures by introducing oxygen into the grain boundaries [7]. They doped the material with oxygen by modifying the PED process by an extra negative

current pulse that is applied immediately after the positive pulse (pulse-reverse-technique; PR-PED). It is expected that during the negative current pulse oxygen evolves at the electrode that collects the nanocrystalline Ni and that by this process the surface of the nanocrystalline particles is oxidised.

The *ex-situ* diffusion experiments were performed at a series of samples that were prepared by PED without  $^{111}\text{In}$ . After deposition, each sample was pre-annealed at a temperature in the range of 670 K to 1470 K (30 min) and subsequently diffused with  $^{111}\text{In}$  at a temperature between 570 K and 670 K (30 min). Finally, the samples were investigated as a function of additional annealing in the temperature range of 670 K to 1470 K.

The experimental investigations, presented here, were performed by perturbed  $\gamma\gamma$ -angular correlation spectroscopy (PAC) using radioactive  $^{111}\text{In}$  probe atoms in order to detect the local magnetic field at the site of the probe atom. The data yield information about local magnetic properties of crystallites and interfaces and about the formation of ferromagnetic or anti-ferromagnetic phases [8]. The probe  $^{111}\text{In}$  decays to an excited level of its daughter isotope  $^{111}\text{Cd}$ , followed by the emission of a  $\gamma_1$ - $\gamma_2$  cascade, which includes the intermediate  $I = 5/2$  nuclear level with a lifetime of  $\tau = 123$  ns. The magnetic hyperfine interaction of the local magnetic field ( $\mathbf{B}_{\text{loc}}$ ) with the nuclear magnetic moment  $\boldsymbol{\mu}$  of the  $I = 5/2$  level effects a modulation of the emission probability of  $\gamma_2$ , if  $\gamma_2$  is detected in coincidence at a fixed angle  $\theta$  with respect to  $\gamma_1$ . The modulation is governed by the Larmor frequency  $\omega_L$ , from which the local magnetic field at the site of the  $^{111}\text{Cd}$  nucleus is obtained by the relation [8]:

$$g \cdot \mu_N \cdot \mathbf{B}_{\text{loc}} = \hbar \cdot \omega_L \quad (\text{Eq. 1})$$

Here,  $\mu_N$  is the nuclear magneton and  $g = -0.3062$  the nuclear g-factor of the  $I = 5/2$  level of  $^{111}\text{Cd}$ . The PAC time spectrum  $R(t)$  is described by

$$R(t) = A_2 \cdot \left[ f \cdot (s_0 + s_1 \cos(\omega_L t) \cdot \exp(-\Delta\omega_L t) + s_2 \cos(2\omega_L t) \cdot \exp(-2\Delta\omega_L t)) + (1-f) \right] \quad (\text{Eq. 2})$$

whereby  $t$  reflects the time passed between the emission of the two  $\gamma$ -quanta. From the  $R(t)$  spectrum the two frequencies  $\omega_L$  and  $2\omega_L$  are extracted yielding  $B_{\text{loc}}$  (Eq. 1). The amplitude  $f$  of the modulation reflects the absolute fraction of probe atoms residing in an environment that produces a particular non-zero magnetic field  $\mathbf{B}_{\text{loc}}$ . The fraction of probe atoms exposed to a zero field is denoted by  $(1-f)$ . In the case of several different environments, characterised by different values of  $\mathbf{B}_{\text{loc}}$ ,  $f$  is split into different fractions  $f_i$ , whereby each fraction is associated with its own characteristic Larmor frequency. In general, a distribution ( $\Delta\omega_L$ ) about the modulation frequencies can be present, which usually is caused by slight perturbations in the vicinity of the probe atom. For

Table 1: Experimental conditions used for the deposition of nanocrystalline Ni samples. ( $T$ : temperature of the electrolyte;  $j^+$ ,  $t(j^+)$ : current density and duration of the positive current pulse;  $j^-$ ,  $t(j^-)$ : current density and duration of the negative current pulse;  $t_{\text{off}}$ : switch-off time)

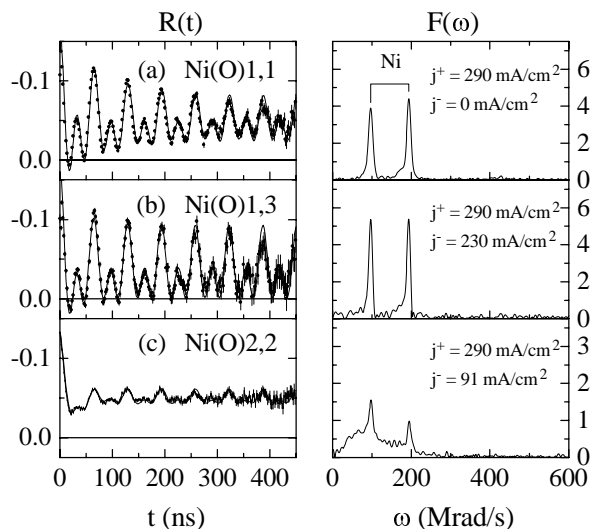
| sample    | anode | electrolyte   | T<br>(°C) | $j^+$<br>(mA/cm <sup>2</sup> ) | $t(j^+)$<br>(ms) | $j^-$<br>(mA/cm <sup>2</sup> ) | $t(j^-)$<br>(ms) | $t_{\text{off}}$<br>(ms) |
|-----------|-------|---|-----------|--------------------------------|------------------|--------------------------------|------------------|--------------------------|
| Ni(O)#1,n | Ni    | NiSO <sub>4</sub> (40g/l),<br>K,Na-tartrate (120g/l),<br>NH <sub>4</sub> Cl (40g/l) | 40        | 290                            | 1                | 0; 182; 230                    | 1                | 48                       |
| Ni(O)#2,n | Pt    |   |           | 290                            | 1                | 0; 91; 137; 182                | 1                | 48                       |
| Ni#1      | Ni    |   |           | 170                            | 1                | -                              | -                | 49                       |

the present experiments a Lorentzian frequency distribution was assumed. A more detailed description of PAC spectroscopy can be found elsewhere [8,9].

## Results and discussion

### 1) Nanocrystalline Ni doped with oxygen

The samples referring to Ni(O)#1 (see Table 1) were deposited by PR-PED using Ni-electrodes. The PAC spectrum in Fig. 1a shows the two components of a magnetic interaction, which are known from earlier investigations on nanocrystalline Ni [10,11,12]: They are attributed to lattice sites of the  $^{111}\text{In}$ -atoms in the core of the crystallites ( $\omega_L = 97.6$  MHz,  $\Delta\omega_L = 0$ ) and in the so called magnetic boundaries ( $\omega_L = 96$  MHz,  $\Delta\omega_L = 5$  MHz). The frequency distribution  $\Delta\omega_L$  causes the relaxation of the modulation amplitude in the  $R(t)$  spectrum in Fig. 1a. With increasing current density of the negative pulse  $j^-$  the fraction of  $^{111}\text{In}$ -atoms on core sites increases at the expense of that at boundary sites (Fig. 1b). There is no indication for the formation of a new crystalline phase containing oxygen. However, it is possible that the negative current pulse was too weak in our experiments [7] in order to incorporate oxygen at a concentration above the detection limit of PAC.



**Fig. 1:** PAC spectra and Fourier transforms of nanocrystalline Ni prepared (a,b) using Ni electrodes (Ni(O)#1) and (c) using a Pt anode (Ni(O)#2).

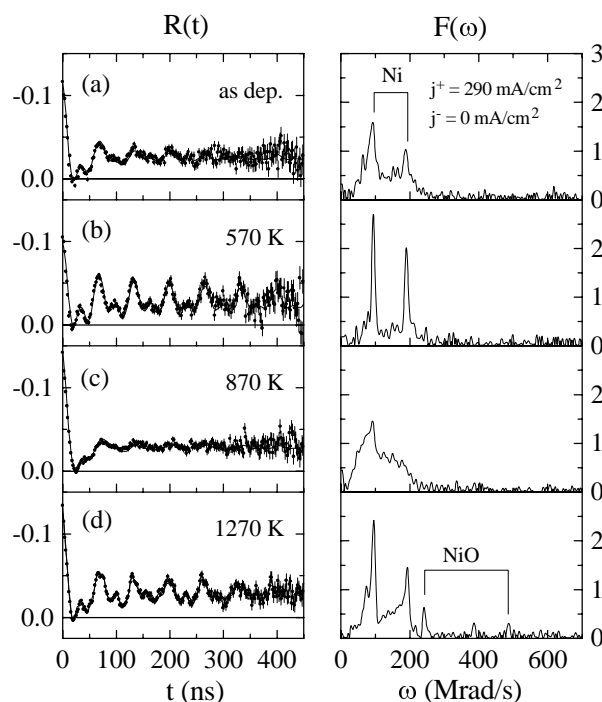
After replacing the Ni anode by a Pt anode (samples Ni(O)#2) a strong modification of the material was observed by PAC: The spectra in Figs. 1c and 2a show a reduced fraction  $f_{\text{Ni}}$  of  $^{111}\text{In}$  atoms on substitutional Ni-sites. In addition, the Larmor-frequency exhibits a strong frequency distribution. Comparing the data in Figs. 1c and 2a it is shown that the application of an additional negative current pulse caused only a weak effect. Annealing of Ni(O)#2 successively at higher temperatures, however, shows a strong temperature dependence of the environment of the  $^{111}\text{In}$ -atoms (Figs. 2 and 3): At temperatures up to 570 K,  $f_{\text{Ni}}$  increases; it decreases between 570 K and 770 K, and above 870 K,  $f_{\text{Ni}}$  increases again. Increasing the annealing temperatures above 870 K, an additional frequency doublet ( $\omega_L = 250$  MHz) is observed (Fig. 2d). By comparison with PAC investigations in NiO, this additional frequency can be assigned to  $^{111}\text{In}$ -atoms located on Ni-sites in anti-ferromagnetic NiO [13]. The additional formation of NiO by annealing at higher temperatures is shown in Fig. 3 (closed symbols). Since the annealing was performed in an evacuated quartz ampoule without breaking the ampoule between the annealing steps, the incorporation of oxygen during the PED process is proven.

Regarding the source of oxygen, we propose the following mechanism: In the electrolyte oxygen is evolved at the Pt anode, thereby enriching the electrolyte with oxygen. Since, the electrolyte is stirred during the whole PED process, the oxygen enriched electrolyte is transported to the cathode. During the deposition of Ni at the cathode, therefore, oxygen can be incorporated into the grain boundaries and also into the Ni grains. On the other hand, the solubility of oxygen in crystalline Ni is very low and, therefore, a supersaturated solution is expected to be formed. As a consequence, oxygen might cause an internal stress within the grains, which can explain the broad frequency distribution about  $\omega_L$  visible in Figs. 1c and 2a. From earlier investigations [10] it is known that in

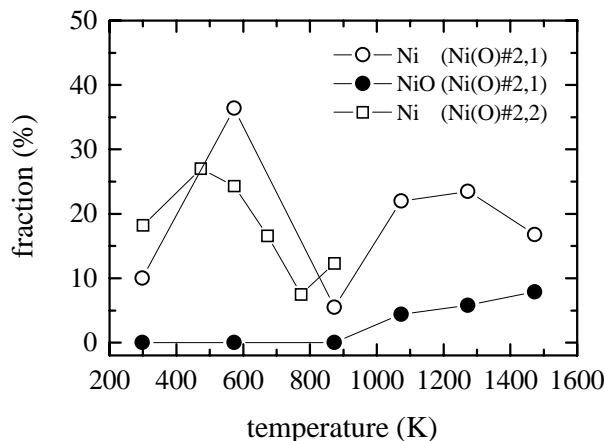
nanocrystalline Ni prepared by PED and doped *in-situ* with  $^{111}\text{In}$  a diffusion of In atoms from grains into grain boundaries does not occur. For the temperature dependence of  $f_{\text{Ni}}$  (Fig. 3, open symbols), therefore, the following interpretation is proposed: Below 570 K, the stress is reduced by local lattice relaxations. At the same time, a weak grain growth may occur. Above 570 K, oxygen becomes mobile, diffuses to the grain boundaries and reduces the concentration of oxygen within the grains. Up to about 800 K, a part of the oxygen atoms is trapped at the  $^{111}\text{In}$  atoms and forms small In-O defect complexes. The strong damping visible in the  $R(t)$  spectrum of Fig. 2c is caused by the superposition of the magnetic interaction and electric field gradients originating from these defect complexes. The majority of oxygen, however, moves to grain boundaries and stabilises the material against grain growth [7]. Above 870 K, the oxygen no longer stabilises the grain boundaries. The grain boundaries start to move leaving the oxygen behind, which now forms precipitates of crystalline NiO. The  $^{111}\text{In}$ -atoms near the grain boundaries are embedded into the NiO precipitates detecting the hyperfine field of anti-ferromagnetic NiO phase. In addition, the In-O complexes in the grains dissociate, leaving the  $^{111}\text{In}$ -atoms on substitutional Ni-sites and, thereby, effecting the new increase of  $f_{\text{Ni}}$ .

## 2) Diffusion of In in nanocrystalline Ni

The incorporation of  $^{111}\text{In}$ -atoms on substitutional Ni-sites of initially nanocrystalline Ni following diffusion was observed to occur in nanocrystalline Ni at lower temperatures than in polycrystalline Ni [12]. The altered diffusion properties compared to polycrystalline material, therefore, reflect altered properties of the nanocrystalline material. The conversion from nanocrystalline to polycrystalline material upon thermal treatment was investigated by PAC pursuing the diffusion behaviour, i.e. the transition of In from the grain boundaries into the grains, as a function of thermal pre-annealing. For this purpose a nanocrystalline Ni samples was produced by PED and subsequently divided into several pieces. One piece was directly diffused with  $^{111}\text{In}$ , the others were pre-annealed at selected temperatures in range 670 K to 1470 K before the diffusion of  $^{111}\text{In}$ . The incorporation of  $^{111}\text{In}$  by diffusion was started at temperatures between 570 K and 670 K. Due to the thermal pre-treatment an average grain size being typical for the respective pre-annealing temperature should be obtained. Subsequently, the samples were heated at temperatures up to 1470 K and after each annealing step a



**Fig. 2:** PAC spectra and Fourier transforms of a Ni sample doped with oxygen (Ni(O)#2,1) and measured (a) after deposition and (b-d) after subsequent annealing at different temperatures.

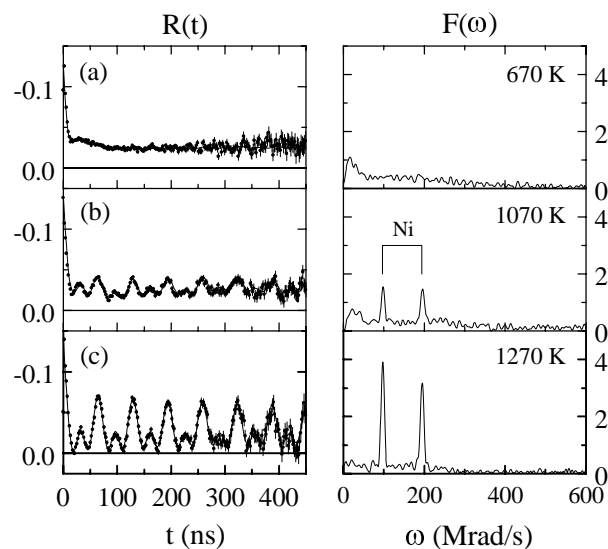


**Fig. 3:** Fractions  $f_{\text{Ni}}$  and  $f_{\text{NiO}}$  of  $^{111}\text{In}$ -atoms on substitutional sites of Ni and NiO, respectively, after annealing of Ni(O)#2.

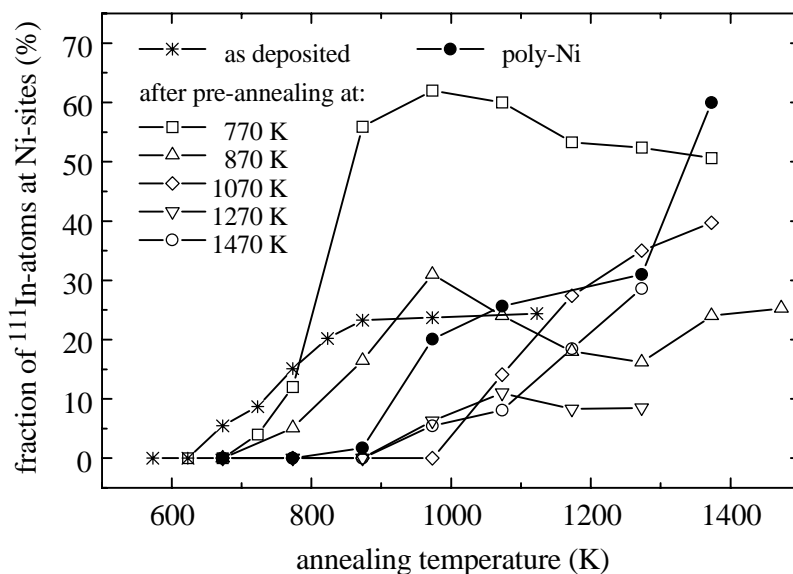
PAC spectrum was recorded at 295 K. As reference, a polycrystalline Ni sample pre-annealed at 1270 K was investigated.

After the first diffusion step (570 - 670 K) for each pre-annealing temperature no well defined frequencies are observed in the PAC spectra (Fig. 4a). It is concluded that the  $^{111}\text{In}$ -atoms are located in grain boundaries, which do not give rise for a unique hyperfine field. The final incorporation of  $^{111}\text{In}$  on substitutional Ni sites in the grains upon subsequent annealing is strongly affected by the pre-annealing temperature. It starts always around the pre-annealing temperature up to a pre-annealing temperature of 1070 K (Figs. 4b and 5). For higher pre-annealing temperatures, the incorporation of the  $^{111}\text{In}$ -atoms on substitutional Ni-sites starts always between 970 K and 1070 K and follows no longer the pre-annealing temperature. The sample that was not pre-annealed before  $^{111}\text{In}$  diffusion, shows the incorporation of the  $^{111}\text{In}$ -atoms on substitutional sites after annealing above 670 K, i.e. near the first diffusion temperature. For comparison, the polycrystalline Ni sample behaves similar to the nanocrystalline Ni samples pre-annealed at temperatures above 1070 K. The fraction of  $^{111}\text{In}$ -atoms on substitutional Ni-sites tends to saturate at high annealing temperatures, but the actual value is not a simple function of the pre-annealing temperature (Fig. 5) and is not yet understood.

Obviously, the incorporation of the  $^{111}\text{In}$ -atoms on substitutional sites inside of the grains is strongly related to the respective pre-annealing temperature. It is concluded that this process is directly correlated with the grain growth, though the individual mean grain size of the samples before  $^{111}\text{In}$ -diffusion was not determined in the present experiments. The absence of sharp frequencies below the pre-annealing temperature (Fig. 4a) is in agreement with an enhanced diffusion of the In-atoms along the grain boundaries. The transfer of the In-atoms from the grain boundaries into the crystallites, which is directly visible via the occurrence of the unique Larmor-frequencies (Figs. 4b and 4c), is obviously not governed by the volume diffusion coefficient because it starts at different temperatures for different pre-annealing temperatures (Fig. 5). Since a renewed grain growth in the sample should start as soon as



**Fig. 4:** PAC spectra measured after diffusion of  $^{111}\text{In}$  into nanocrystalline Ni (Ni#1) and subsequent annealing at different temperatures. The sample was pre-annealed at 1070 K.



**Fig. 5:** Fraction  $f_{\text{Ni}}$  of  $^{111}\text{In}$ -atoms incorporated on substitutional Ni sites in nanocrystalline Ni during isochronal annealing. Plotted are the results for samples pre-annealed at the indicated temperatures.

the annealing temperature passes the pre-annealing temperature of the respective sample and since the grain growth is necessarily connected with moving grain boundaries, it is suggested that the In-atoms are left behind the moving grain boundaries on substitutional Ni sites. Such a process was discussed by Mishin et al. using the example of the diffusion of Ni and Co in Nb [14]. There, the shape of the diffusion profile was determined with help of the tracer diffusion technique and the data were fitted to a model assuming moving grain boundaries. The tracer diffusion technique, however, yields no direct information about the actual lattice sites of diffusing impurity atoms. In contrast, the PAC experiments do not yield information about the diffusion profile but they give direct information about the location of the diffusing In-atoms. Thus, the information obtained by both techniques is complementary. Regarding the grain growth of initially nanocrystalline Ni the data in Fig. 5 suggest that the conversion to polycrystalline material is spread over a wide temperature range and is completed just at a pre-annealing temperature of about 1070 K.

## Conclusion

The stabilisation against grain growth upon thermal treatment was investigated by PAC on nanocrystalline Ni samples prepared by PED. A significant incorporation of oxygen was observed by using a Pt anode during the PED process. The PAC data suggest a stabilisation of the Ni grains up to an annealing temperature of about 800 K. By studying the diffusion of In atoms in nanocrystalline Ni and assuming that the incorporation into the Ni grains is governed by moving grain boundaries, it can be stated that the conversion from nanocrystalline to polycrystalline Ni occurs up to a pre-annealing temperature of about 1070 K.

*The financial support by the DFG within the SFB 277 is acknowledged.*

---

## References

- [1] D. Osmola, E. Renaud, U. Erb, L. Wong, G. Palumbo, and K.T. Aust, *Mat. Res. Soc. Symp. Proc.* 286 (1993), p. 191
- [2] H. Natter, M. Schmelzer, S. Janßen, and R. Hempelmann, *Ber. Bunsenges. Phys. Chem* 101 (1997), p. 1706
- [3] H. Natter, M. Schmelzer, and R. Hempelmann, *J. Mater. Res.* 13 (1998), p. 1186
- [4] H. Kisker, T. Gessmann, R. Würschum, H. Kronmüller, and H.-E. Schaefer, *Nanostructured Materials* 6 (1995), p. 925
- [5] J.F. Löffler, J.P. Meier, B. Doudin, J.-P. Ansermet, and W. Wagner, *Phys. Rev.* B57 (1998), p. 2915
- [6] U. Erb, *Nanostructured Materials* 6 (1995), p. 533
- [7] H. Natter, private communication, A. Dierstein, H. Natter, H.-O. Stephan, C. Kropf and R. Hempelmann, to be presented on the Nano2000 conference and published in *Scripta Materialia*
- [8] Th. Wichert and E. Recknagel, in *Microscopic Methods in Metals*, ed. U. Gonser, *Topics in Current Physics* 40 (1986), p. 317
- [9] T. Butz, *Hyp.Int.* 52 (1989), p. 189
- [10] St. Lauer, Z. Guan, H. Wolf, H. Natter, M. Schmelzer, R. Hempelmann, and Th. Wichert *Nanostructured Materials* 12 (1999), p. 955
- [11] St. Lauer, Z. Guan, H. Wolf, and Th. Wichert, *Hyperfine Interactions*, 120/121 (1999), p. 307
- [12] H. Wolf, Z. Guan, St. Lauer, H. Natter, M. Schmelzer, R. Hempelmann, and Th. Wichert, *Journal of Metastable and Nanocrystalline Materials* 8 (2000), p. 847
- [13] Th. Wenzel, M. Uhrmacher, and K.P. Lieb, *J. Phys. Chem.* 55 (1994), p. 683
- [14] Y. Mishin, Chr. Herzig, J. Bernardini, and W. Gust, *International Materials Review* 42 (1997), p. 155