

# NANOSCALE HYDROGEN STORAGE MATERIALS STUDIED BY TEM

M. Makowiecka<sup>1</sup>, L. Kepinski<sup>2</sup> and M. Jurczyk<sup>1</sup>

<sup>1</sup>Institute of Materials Science and Engineering, Poznan University of Technology, Skłodowska-Curie 5 Sq., 60-695 Poznan, Poland

<sup>2</sup>Institute of Low Temperature and Structure Research, Trzebiatowski Institute, Polish Academy of Sciences, Okolna 2, 50-422 Wrocław, Poland

Received: March 29, 2008

**Abstract.** Nanoscale TiNi-type hydrogen storage material has been prepared by mechanical alloying (MA). The properties of so produced alloys were studied by XRD and TEM. These studies showed that, firstly, after 20 h of milling, the starting mixture of the elements had transformed almost into an amorphous phase and, secondly, the annealing in high purity argon at 700 °C for 0.5 h led to formation of the CsCl-type structures with a crystallite sizes of about 4-30 nm. Additionally, the effect of Zr on the structure and electrochemical properties of nanocrystalline TiNi-type alloys was investigated. It was found that the respective replacement of Ni in nanocrystalline TiNi by Zr improved not only the discharge capacity but also the cycle life of these electrodes.

## 1. INTRODUCTION

During last years, interest in the study of nanoscale materials has been increasing. This is due to recent advances in materials' synthesis and the realization that these materials exhibit many interesting and unexpected physical as well as chemical properties with a number of potential technological applications. For example, hydrogen storage nanomaterials are the key to the future of the storage and batteries/cells industries [1-3].

Nanoscale hydrogen storage materials can be produced by mechanical alloying [1-4]. During the MA process, the powder particles are periodically trapped between colliding balls and are plastically deformed. Such a feature occurs by the generation of a wide number of dislocations as well as other lattice defects. Furthermore, the ball collisions cause fracturing and cold welding of the elementary particles, forming clean interfaces at the atomic scale. Further milling lead to an increase of the interface number and the sizes of the elementary

component area decrease from millimeter to submicrometer lengths. Concurrently to this decrease of the elementary distribution, some nanocrystalline intermediate phases are produced inside the particles or at its surfaces. As the milling duration develops, the content fraction of such intermediate compounds increases leading to a final product whose properties are the function of the milling conditions.

Among the different types of hydride forming compounds, TiNi-type alloys are among the most promising electrode materials for nickel-metal hydride (Ni-MH) batteries. The microcrystalline TiNi system has been widely studied in the past [5-8]. TiNi alloy, which crystallizes in the cubic CsCl-type structure, can absorb up to 1 H/f.u. at room temperature.

To improve the activation of this alloy several approaches have been adopted. For example, high-energy ball-milling (HEBM) is effective for the improvement of the initial hydrogen absorption rate,

Corresponding author: M. Makowiecka, e-mail: makmar@sol.put.poznan.pl

**Table 1.** Lattice constants before and after hydrogenation and discharge capacities on 15<sup>th</sup> cycle for TiNi-type alloys produced by MA and annealing (700 °C/0.5 h).

Lattice constants	TiNi	TiNi <sub>0.875</sub> Zr <sub>0.125</sub>
$a[\text{Å}]$	3.018	3.029
$a_H[\text{Å}]$	3.142	3.156
Discharge capacity on 15 <sup>th</sup> cycle [mA h g <sup>-1</sup> ]	79	134

due to the reduction in the particle size and the creation of new clean surfaces [1]. The synthesis of nanocrystalline TiFe<sub>1-x</sub>Ni<sub>x</sub> (0 ≤ x ≤ 1) alloys by MA process has been published [9,10], as well. Materials obtained by the substitution of Ni for Fe in TiFe<sub>1-x</sub>Ni<sub>x</sub> lead to great improvement in activation behaviour of the electrodes.

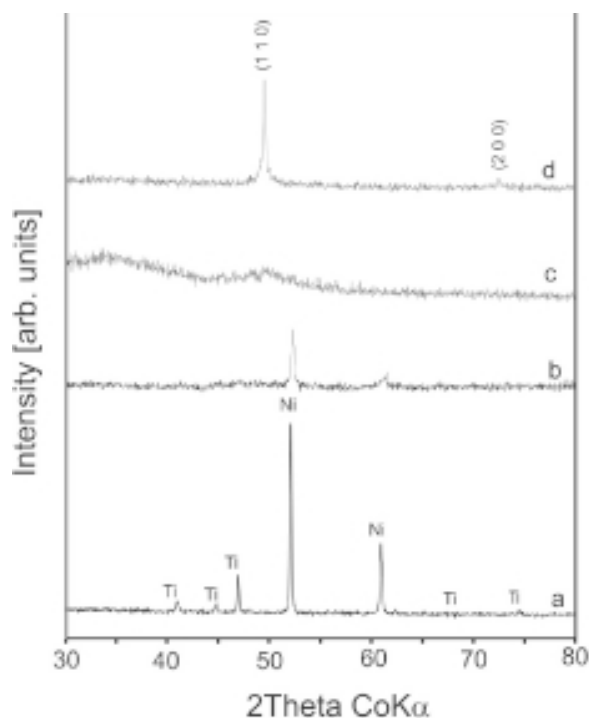
In this work, we have prepared nanocrystalline TiNi-type hydrogen storage alloys. The properties of these materials were investigated by XRD and TEM. Additionally, the Zr was substituted for nickel in TiNi and the structural and electrochemical properties were studied.

## 2. EXPERIMENTAL

Mechanical alloying was performed under argon atmosphere using a SPEX 8000 Mixer Mill. The purity of the starting materials was at least 99.8% and the composition of the starting powder mixture corresponded to the stoichiometry of the “ideal” reactions. The elemental powders (Ti: ≤45 μm, Ni: 3-7 μm, Zr: ≤150 μm) were mixed and poured into the vial. The mill was run up to 20 h for every powder preparation. The as-milled powders were heat treated at 700 °C for 0.5 h under high purity argon to form ordered phases. The powders were characterized, at the various stages during milling, prior to annealing and after annealing, by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM). The mechanically alloyed materials, in nanocrystalline forms, with 10 wt.% addition of Ni powder, were subjected to electrochemical measurements as working electrodes [9].

## 3. RESULTS AND DISCUSSION

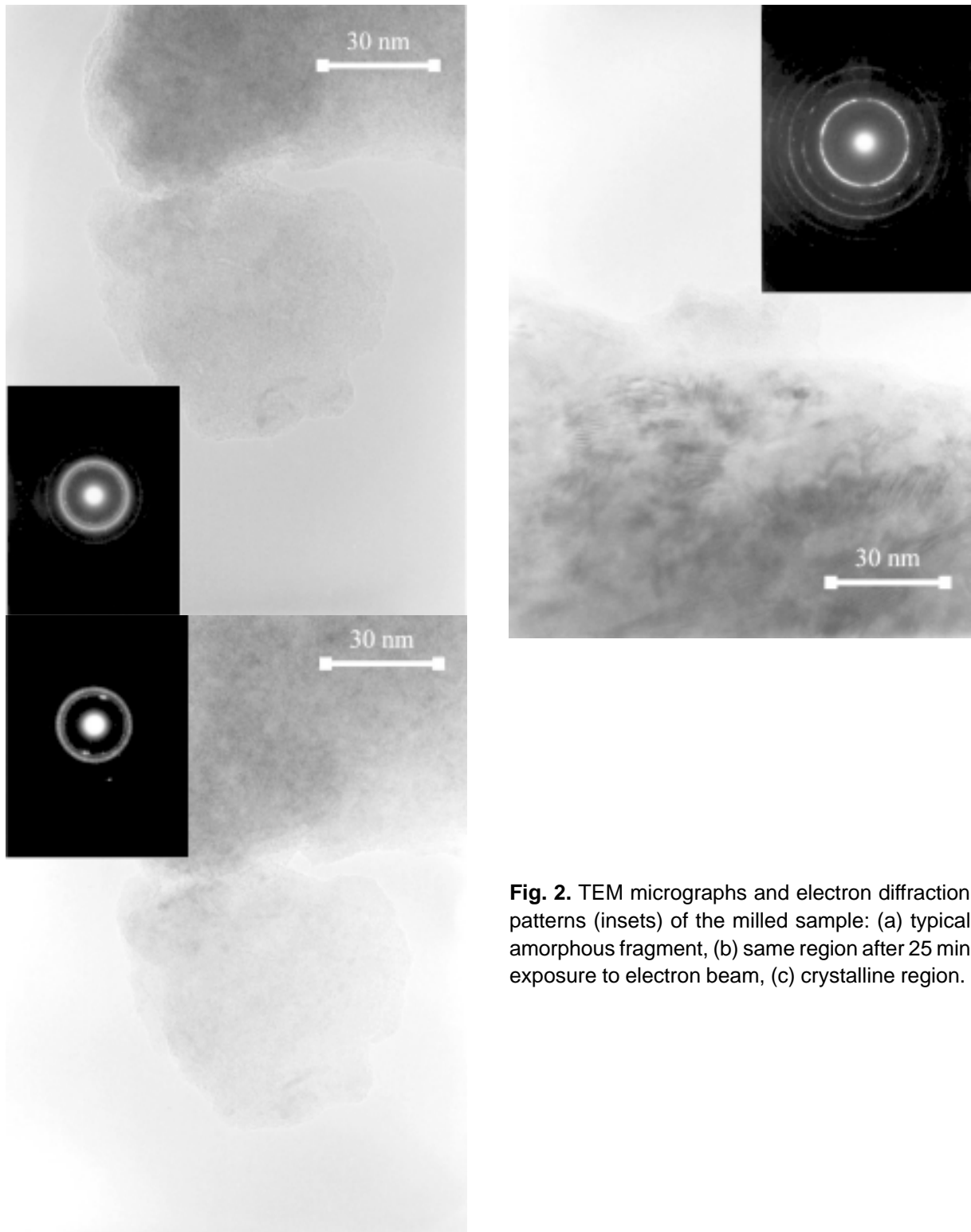
The effect of MA processing was studied by X-ray diffraction, TEM as well as by electrochemical



**Fig. 1.** XRD spectra of a mixture of Ti and Ni powders mechanically alloyed for different times: (a) 0 h, (b) 3 h, (c) 5 h, and (d) after annealing 700 °C/0.5 h.

measurements. In the present study, TiNi-type alloys have been prepared by mechanical alloying followed by annealing (see text for details). During mechanical alloying the originally sharp diffraction lines of Ti and Ni gradually become broader and their intensity decreases with increasing milling time (Fig. 1). The powder mixture milled for more than 5 h has transformed completely to an amorphous phase. The milled powder is finally heat treated to obtain the desired microstructure and properties. Formation of the nanocrystalline alloys was achieved by annealing of the amorphous material in high purity argon atmosphere at 700 °C for 0.5 h. The diffraction peaks were assigned to those of CsCl-type structure with a cell parameter  $a = 3.018 \text{ Å}$  (Fig. 1d, Table 1).

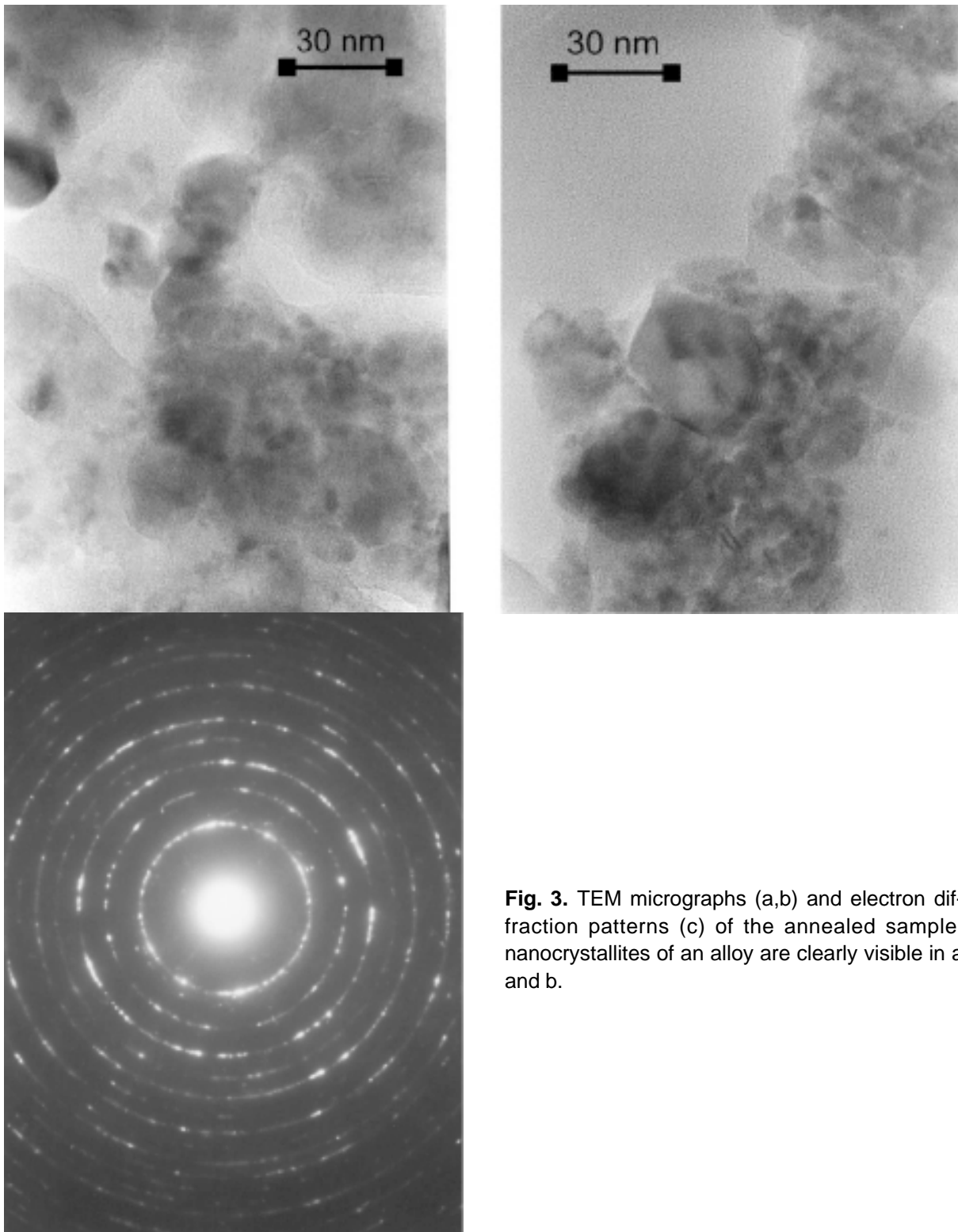
Microstructure and possible local ordering in the samples was studied by TEM. The sample milled for 5 h was mostly amorphous as appears from a high resolution image (Fig. 2a). SAED pattern (see inset to Fig. 2a) contains broad rings at positions expected for TiNi with CsCl structure. There are, however additional weak, diffuse rings, most prob-



**Fig. 2.** TEM micrographs and electron diffraction patterns (insets) of the milled sample: (a) typical amorphous fragment, (b) same region after 25 min exposure to electron beam, (c) crystalline region.

ably from  $\text{TiO}_2$ . It has been found that the amorphous alloy was unstable upon exposure to electron beam and underwent some crystallization. In

the image acquired after 25 min exposure to the beam (Fig. 2b) formation of an ordered regions (defined as patches with parallel lattice fringes) is



**Fig. 3.** TEM micrographs (a,b) and electron diffraction patterns (c) of the annealed sample; nanocrystallites of an alloy are clearly visible in a and b.

seen. Accordingly, additional sharp reflections appear in the SAED pattern (inset to Fig. 2b). Apart from prevailing amorphous phase, the milled

sample contained small amount of crystalline alloy with CsCl structure (Fig. 2c). Lack of any sharp reflections in the XRD pattern (cf. Fig. 1b) suggests

that the amount of the crystalline phase is very low and/or it forms during in TEM observation.

Microstructure of the annealed sample is shown in Fig. 3. Analysis of high resolution images (Figs. 3a and 3b) revealed the presence of well developed crystallites with broad range of sizes from 4 up to more than 30 nm. SAED pattern obtained from large area (200  $\mu\text{m}$ ) (Fig. 3c) contains sharp rings corresponding to an alloy with CsCl structure.

Table 1 reports the discharge capacities of the studied nanocrystalline TiNi-type materials. As shown earlier, nanocrystalline powders have a larger capacity than the amorphous parent alloy materials [3]. Annealing leads to grain growth, release of microstrain and to an increase of the storage capacity. This behaviour is due to a well-established diffusion path for hydrogen atoms along the numerous grain boundaries. The discharge capacity of the electrodes prepared by application of MA TiNi alloy powder is low. Materials obtained by the substitution of Ni for Zr in TiNi lead to great improvement in activation behaviour of the electrodes. In the annealed nanocrystalline  $\text{TiNi}_{0.875}\text{Zr}_{0.125}$  powder, discharge capacity of up to 135 mA h  $\text{g}^{-1}$  was measured. The electrodes mechanically alloyed and annealed from the elemental powders displayed maximum capacities at around the 3-rd cycle but degraded slightly with cycling. Generally, it was accepted that the oxidation and segregation of titanium were prominent factors associated with the capacity loss during charge-discharge cycling [7]. The alloying elements Zr, substituted simultaneously for nickel atoms in nanocrystalline TiNi master alloy prevented oxidation of this electrode material. In this annealed nanocrystalline powder discharge capacities up to 158 mA h  $\text{g}^{-1}$  were measured.

Application of titanium alloys as hydrogen storage materials focused our attention also on the electronic structure of nanocrystalline TiNi and its modification by Zr and Fe atoms [10]. The significant broadening of the valence band for the nanocrystalline TiNi based alloys could be explained by a strong deformation of the nanocrystals. Normally the interior of the nanocrystal is contracted and the distances between atoms located at the grain boundaries are expanded [11]. Furthermore, in the case of MA nanocrystalline  $\text{TiNi}_{0.875}\text{Zr}_{0.125}$  alloy the Ni atoms could also occupy metastable positions in the deformed grain. The above behaviour can also modify the electronic structure of the valence band. As a result the strong modifi-

cations of the electronic structure of the nanocrystalline TiNi-type alloys compared to that of microcrystalline materials could significantly influence their hydrogenation properties.

#### 4. CONCLUSION

In conclusion, nanocrystalline TiNi-based alloys synthesized by mechanical alloying and annealing were used as negative electrode materials for Ni-MH battery. The effect of MA processing was studied by XRD and TEM. These studies showed that, firstly, after 20 h of milling, the starting mixture of the elements had transformed almost into an amorphous phase and, secondly, the annealing in high purity argon at 700 °C for 0.5h led to formation of the CsCl-type structures with a crystallite sizes of about 4-30 nm. It was found that the respective replacement of Ni in TiNi by Zr improved not only the discharge capacity but also the cycle life of these electrodes. The studies shows, that nanoscale hydrogen storage material can be produced by MA process and the electrochemical properties of Ni-MH batteries are a function of the microstructure and the chemical composition of the used electrode materials.

#### ACKNOWLEDGEMENTS

The partial financial support of the Polish National Committee for Scientific Research under the contract No Nr 3 T10A 033 29 is gratefully acknowledged.

#### REFERENCES

- [1] L. Zaluski, A. Zaluska and J.O. Ström-Olsen // *J. Alloys Comp.* **253-254** (1997) 70.
- [2] A. Anani, A. Visintin, K. Petrov, S. Srinivasan, J.J. Reilly, J.R. Johnson, R.B. Schwarz and P.B. Desch // *J. Power Source* **47** (1994) 261.
- [3] M. Jurczyk // *Bull. Pol. Ac.: Tech.* **52** (2004) 67.
- [4] M. Jurczyk, L. Smardz and A. Szajek // *Mat. Sc. Eng. B* **108** (2004) 67.
- [5] J.J. Reilly // *Z. Phys. Chem.* **117** (1979) 155.
- [6] M.H. Mintz, S. Vaknin, S. Biderman and Z. Hadari // *J. Appl. Phys.* **52** (1981) 463.
- [7] C.S. Wang, Y.Q. Lei and Q.D. Wang // *J. Power Sources* **70** (1998) 222.
- [8] M. Jurczyk, E. Jankowska, M. Nowak and J. Jakubowicz // *J. Alloys Comp.* **336** (2002) 265.

- [9] M. Makowiecka, E. Jankowska, I. Okonska and M. Jurczyk // *J. Alloys Comp.* **388** (2005) 303.
- [10] A. Szajek, M. Makowiecka, E. Jankowska and M. Jurczyk // *J. Alloys Comp.* **403** (2005) 323.
- [11] M.R. Fitzsimmons, J.A. Estman, R.A. Robinson, A.C. Lawson, J.D. Thompson and R. Morshovich // *Phys. Rev. B* **48** (1993) 8245.