*Materials Science-Poland, Vol. 24, No. 3, 2006*

# Electronic and magnetic properties of metastable $Fe_{22}PdB_6$ and $Fe_{22}PtB_6$ compounds

A. SZAJEK, S.A. KOSTYRYA, B. IDZIKOWSKI*

Institute of Molecular Physics, Polish Academy of Sciences,
M. Smoluchowskiego 17, 61-179 Poznań, Poland

Nanostructured soft magnets are examples of materials that are made by the partial crystallization of amorphous precursors. $Fe_{22}(Pt,Pd)B_6$ compounds, which crystallize in the $Cr_{23}C_6$-type structure and have four inequivalent sites (4a, 8c, 48h, 32f) for Fe, Pd, and Pt atoms, can form grains of several nanometers in diameter in a residual amorphous matrix. Band structure calculations show that the local magnetic moments of Fe atoms depend on their local environments, and for 4a and 8c sites the resultant moments are enhanced up to about $2.5–3\mu_B$/atom. Pd and Pt atoms prefer to be located in the 4a and 8c positions, respectively. Magnetic moments induced on the substituted atoms are equal to $0.45\mu_B$/atom on the Pt atom and $0.39\mu_B$/atom on Pd.

Key words: *amorphous alloy; electronic structure; magnetic moment*

## 1. Introduction

Amorphous Fe-based alloys are subject to intensive investigations, because of their interesting properties. Many of them exhibit excellent soft magnetic properties [1] and are very promising materials from the practical point of view. High saturation induction and low coercivity combined with good corrosion resistance [2] make amorphous Ni-based alloys (or with Ni additions) very attractive for a variety of applications. For instance, melt-spun $(Fe_{100-x}Ni_x)_{93-y}Zr_7B_y$ alloys can be used as shape memory materials [3] based on the martensitic transformation from γ-austenite to α-martensite recently studied in this system.

Annealing Ni-based amorphous precursors, e.g. with a chemical composition of $Ni_{64}Fe_{16}Zr_7B_{12}Au$, favours the emergence of cubic $Fe_xNi_{23-x}B_6$ nanocrystalline grains, the metastable phase of which does not exists as a bulk material. The grains are isostructural with $Cr_{23}C_6$ (space group $Fm\bar{3}m$), revealing rather high values of saturation magnetization in the amorphous as well as nanocrystalline states [4].

---

* Corresponding author, e-mail: idzi@ifmpan.poznan.pl

Nanocrystalline soft magnetic samples can be prepared from fully amorphous alloys with special compositions. As a general rule, introducing a so-called inhibitor of grain growth into the alloy is necessary. Controlled annealing in a protective atmosphere favours the emergence of the nanocrystalline phase or phases. The phases can be identified by X-ray diffraction, transmission electron microscopy, or by Mössbauer spectrometry [4]. Various contents of nanocrystals are easily obtained by varying the temperature of isochronal annealing (usually 1 hour) or by special combinations of time/temperature annealing and heating rates.

The temperature dependences of magnetic parameters corresponding to nanosized grains deviate from those of bulk alloys with the same composition. Two mechanisms responsible for the observed effects are proposed: (i) the influence of impurities in nanograins, and (ii) grain surface contribution. The latter plays a non-negligible role, especially when the grain size is of the order of tens of nanometres. The former effect seems to be of minute importance. Different magnetic behaviours may be observed for low, medium, and high volumetric fractions of crystallites.

Band structure calculations showed that the local magnetic moments of Fe, Ni, and Co atoms in $(FeNiCo)_{23}B_6$ compounds depend on their local environments (see Ref. [6] and references therein). Investigations of $Fe_{22}(Pd,Pt)B_6$ alloys are a part of our studies of the magnetic properties of $Fe_{23}B_6$-type alloys. In this paper, we determine the magnetic behaviour of Pd and Pt additions and their site preference based on *ab initio* band structure calculations.

## 2. Method of calculation

Band structures and magnetic moments were calculated using the spin-polarized tight-binding linear muffin-tin orbital (TB LMTO) method in the atomic sphere approximation (ASA) [7, 8]. The overlap volumes of the muffin-tin spheres for both structures were equal to 9.8%. Standard combined corrections for overlapping [7] were used to compensate for errors due to the ASA. Spin-orbit interactions were taken into account in the form proposed by Min and Jang [9]. The von Barth–Hedin [10] potential and experimental values of the lattice constants were used in the calculations. Self-consistent calculations were carried out for 4096 *k*-points in the Brillouin zone. The tetrahedron method was used to integrate over the Brillouin zone [11]. Iterations were repeated until the energy eigenvalues change for consecutive steps was below 0.01 mRy.

## 3. Results and discussion

The results of the band structure calculations are summarized in Fig. 1 as the total densities of electronic states (DOS) for up and down spins. The shapes of local DOS plots depend on the type of atom, its localization, and local environment. The values

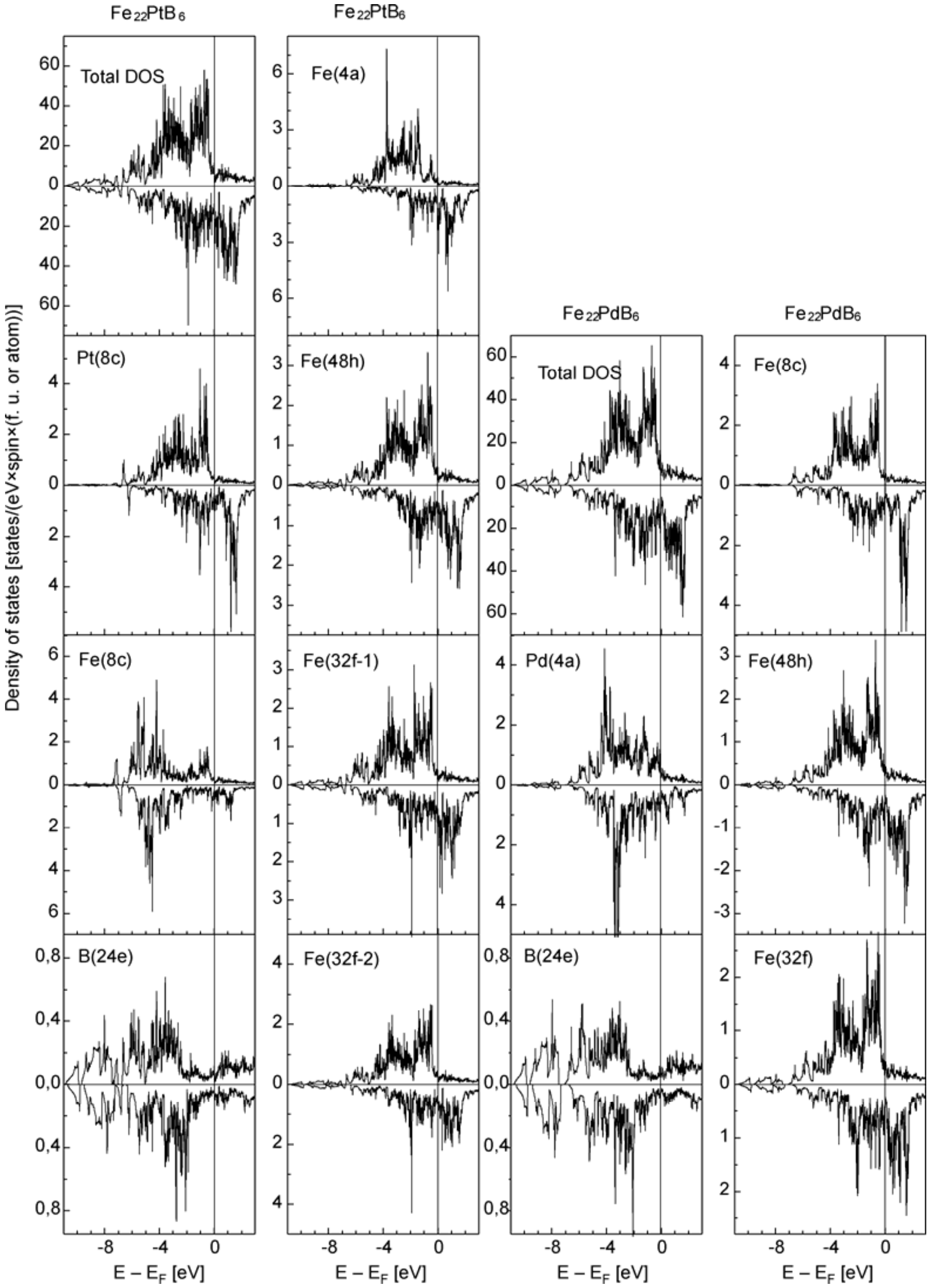

Fig. 1. The total (calculated per f. u.) and local DOS functions for $Fe_{22}(Pt,Pd)B_6$ systems

of the total DOS at the Fermi level ($E_F$) are equal to 14.99 and 22.76 states/(eV·f. u.) for $Fe_{22}PdB_6$ and $Fe_{22}PtB_6$, respectively. Fe(3d), Pd(4d), and Pt(5d) electrons provide the main contribution to the DOS($E = E_F$), about 90%. The site and spin projected values are collected in Table 1, which also contains the calculated saturation magnetic moments.

Table 1. Spin projected (↑, ↓) DOS [states/(eV·spin·atom)] at the Fermi level and calculated local magnetic moments $m$ for Fe, Pd, Pt, and B atoms [$\mu_B$/atom] in $Fe_{22}(Pt,Pd)B_6$

| Compound | Atoms | DOS ↑ | DOS ↓ | $m$ | Compound | Atoms | DOS ↑ | DOS ↓ | $m$ |
|---|---|---|---|---|---|---|---|---|---|
| $Fe_{22}PtB_6$ | Fe(4a) | 0.340 | 1.466 | 3.02 | $Fe_{22}PdB_6$ | Pd(4a) | 0.262 | 0.459 | 0.39 |
| | Fe(8c) | 0.294 | 0.500 | 2.53 | | Fe(8c) | 0.183 | 0.407 | 2.53 |
| | Pt(8c) | 0.285 | 0.262 | 0.45 | | Fe(48h) | 0.215 | 0.414 | 2.23 |
| | Fe(48h) | 0.394 | 0.501 | 2.27 | | Fe(32f) | 0.204 | 0.422 | 1.91 |
| | Fe(32f-1) | 0.351 | 0.743 | 2.00 | | B(24e) | 0.048 | 0.041 | -0.17 |
| | Fe(32f-2) | 0.365 | 0.543 | 1.95 | | | | | |
| | B(24e) | 0.093 | 0.051 | -0.17 | | | | | |
| | Total (per f. u.) | 9.069 | 13.690 | 48.02 | | Total (per f. u.) | 5.128 | 9.863 | 46.47 |

Note that since Pd atoms are located in the 8c site, broken symmetry causes the appearance of additional inequivalent atoms in the 32f position, marked as 32f-1 and 32f-2.

Especially high values of magnetic moments are located on Fe(4a) and Fe(8c) atoms, higher than for bulk bcc-Fe. The magnetic moments depend on local environment, namely (i) the types of neighbours and (ii) interatomic distances. In the case of the 4a and 8c positions, interatomic distances are larger than for *bcc*–Fe and lead to larger Wigner–Seitz (WS) radii and consequently larger magnetic moments. These data can be interpreted qualitatively as showing a tendency toward the localization of d electrons [12]. With increasing WS radii, the magnetic moments approach values closer to the moment of an isolated Fe atom. An increasing number of neighbouring boron atoms reduces the magnetic moment of iron. Band structure calculations were performed for all possible configurations of Pd and Pt impurities in the unit cell. A direct comparison of the calculated total energies gave the site preference of impurities. Table 1 contains values for the positions of the impurities that minimize the total energies. Pd and Pt atoms prefer 4a and 8c positions, respectively. Although metallic palladium and platinum are nonmagnetic, in this case quite large magnetic moments are induced on these additions, 0.45$\mu_B$/atom on Pt atoms and 0.39$\mu_B$/atom on Pd. The WS radius used in calculations for Pd in the 4a site was about 1.7 Å, 8.6% larger than for the Pd-fcc metallic system. The influence of the lattice constant on the magnetic moment of Pd has been considered by other researchers [13–15]. In their calculations, sudden phase transitions from a nonmagnetic to a ferromagnetic state were observed for lattice constants larger than the equilibrium value by about 5.5–10%.

## 4. Conclusions

Nanocrystalline $Fe_{22}(Pt,Pd)B_6$ grains created by devitrification in soft magnets could be the reason for the enhancement of their magnetic properties (e.g., saturation and/or remanence magnetization) which is useful in applications. Band structure calculations showed that the local magnetic moments of Fe atoms in $Fe_{22}(Pt,Pd)B_6$ depend on their local environments. In 4a and 8c sites, the resultant Fe moments are enhanced up to about 2.5–3$\mu_B$/atom. Pd and Pt atoms prefer, in the $Cr_{23}C_6$type structure, the 4a and 8c positions, respectively. The magnetic moments induced on the substituted atoms are equal to 0.45$\mu_B$/atom for Pt and 0.39$\mu_B$/atom for Pd.

## References

[1] HASEGAWA R., Mater. Sci. Eng., A 375-377 (2004), 90.
[2] BOZORTH R.M., *Ferromagnetism*, IEEE Press, New York, 1993, p. 102.
[3] GRRER A.L., WALKER I.T., J. Non-Cryst. Solids., 317 (2003), 78.
[4] IDZIKOWSKI B., SZAJEK A., GRENECHE J.-M., KOVAČ J., Appl. Phys. Lett., 85 (2004), 1392.
[5] KOSTYRYA S.A., ŚNIADECKI Z., IDZIKOWSKI B., phys. stat. sol. (b), 242 (2005), 621.
[6] IDZIKOWSKI B., SZAJEK A., Czech. J. Phys. 54 Suppl. D (2004), D59.
[7] ANDERSEN O.K., JEPSEN O., ŠOB M., in *Electronic Structure and Its Applications*, M.S. Yussouff (Ed.), Springer-Verlag, Berlin, 1987, p. 2.
[8] KRIER G., JEPSEN O., BURKHARDT A., ANDERSEN O.K., *The TB-LMTO-ASA program* (source code, version 4.7).
[9] MIN B.I., JANG Y.-R., J. Phys. Cond. Matter, 3 (1991), 5131.
[10] VON BARTH U., HEDIN L., J. Phys. C, 5 (1972), 1629.
[11] BLÖCHL P., JEPSEN O., ANDERSEN O.K., Phys. Rev. B, 49 (1994), 16223.
[12] BAGAYOKO D., CALLAWAY J., Phys. Rev. B, 28 (1983), 5419.
[13] CHEN H., BRENER N.E., CALLAWAY J., Phys. Rev. B, 40 (1989), 1443.
[14] MORUZZI V.L., MARCUS P.M., Phys. Rev. B, 39 (1989), 471.
[15] FRITSCHE L., NOFFLKE J., ECKARDT H., J. Phys. F, 17 (1987), 943.

*Received 1 June 2005*
*Revised 10 October 2005*