Magnetic and magneto-volume properties of Fe$_x$M$_{100-x}$ solid solutions with M=Pd and Pt

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Abstract: Band structure calculations were performed on Fe$_x$M$_{100-x}$ solid solutions with M=Pd and Pt as well as on ordered phases present in the above systems. The equilibrium values of lattice parameters, magnetic moments, Curie temperatures, and spontaneous volume magnetostrictions were computed. A good agreement with experimental results has been shown. The magnetic properties, in particular Curie temperatures, were correlated with distances between iron atoms, as suggested by Néel-Slater curve.

1. Introduction

The Fe-Pd and Fe-Pt alloys systems have a rather complex phase diagrams [1]. Thus, in case of Fe-Pd one, at high temperatures, below solidus line, the presence of $\gamma$-Fe$_x$Pd$_{100-x}$ solid solutions, having fcc type structure, is shown in all the composition range. At room temperature, the $\alpha$-Fe$_x$Pd$_{100-x}$ alloys, having bcc-type structure have been reported for $x \geq 70$ and fcc-type lattice for $x \leq 60$ [2]. In the compositions range $70 \leq x \leq 75$, four phases with different tetragonal distortions, following a Bain transformation path, from fcc to bcc-type lattice, have been reported [3]. When decreasing temperature, the alloys having compositions around $x=50$ and 25 at % Fe, exhibit a typical atomic disorder-order process. The disordered fcc-type alloys, with $40 \leq x \leq 50$, having low magnetic anisotropy, orders to tetragonal L1$_0$-type structure. The ordered FePd$_3$ phase crystallizes in L1$_2$-type structure having $Pm\bar{3}m$ space group. This phase can exist, at room temperature, in the composition range $14 \leq x \leq 38$ [1]. In the phase diagram of Fe-Pt system, the presence of three ordered compounds Fe$_3$Pt, FePt and FePd$_3$ was shown [1].

The magnetic properties of Fe$_x$Pd$_{100-x}$ alloys were experimentally studied [2,4-10]. In the composition range $20 \leq x \leq 70$, the resultant magnetizations decrease linearly with increasing Pd content [4]. The Curie temperatures, $T_c$, have a maximum at $x=50$. The $T_c$ values of the atomic ordered alloys having $40 \leq x \leq 50$ at % Fe, decrease by $\approx 50$ K, as compared to disordered phases [10]. Magnetic neutron scattering on Fe$_x$Pd$_{100-x}$ alloys with $10 \leq x \leq 15$ showed satellite diffuse peaks at $1 \pm \delta$, 0, 0. The wave vector of spin modulation varied with iron concentration. The oscillatory spin component homogeneously coexist with the ferromagnetic long-range order [9]. The effects of pressure on the Curie temperatures of $\gamma$-Fe$_x$Pd$_{100-x}$ with $66 \leq x \leq 72$ were also reported [8]. The $T_c$ values decreased with pressure, while the changes of magnetizations, at 4.2 K, were small.

Band structure calculations were performed on some Pd-Fe alloys, particularly on those atomic ordered, having equatomic composition. There are only few studies on the electronic structure of Fe$_x$Pd$_{100-x}$ solid solutions [11,12]. The electronic structures and the magnetic properties of Fe$_x$Pd$_{100-x}$ alloys with $50 \leq x \leq 85$ were investigated in the framework of density functional theory using the full potential approximation [11]. The Körtinga-Kohn-Rostoker Green’s function method, with local density functional approximation, was used to obtain the
effects of dilute substitutions of Pd in bcc Fe, on their magnetic properties.

Recently [13], we reported the band structure calculations performed on Fe-Pt alloys and compounds, where a review on previous experimental studies, including band structure calculations, were given. Consequently, in the following we focus mainly on the results obtained by band structure calculations on Fe-Pd system.

2. Computational method

The ground state electronic structures, total energies, magnetic properties and spontaneous volume magnetostriction, of $\alpha$- and $\gamma$-Fe$_x$Pd$_{100-x}$ disordered alloys, as well as on FePd and FePd$_3$ ordered compounds, as in case of Fe-Pt system [13], have been studied by means of spin polarized and scalar relativistic tight-binding linear muffin tin orbital method (TB-LMTO), within atomic sphere approximation (ASA), together with coherent potential approximation (CPA) [14,15]. The LSDA was used for the exchange correlation potential of the electron gas, assuming the Vosko-Wilk-Nussair parameterization [16]. All band structure calculations have been performed by using a mesh of 24x24x24 k-points in the full Brillouin zone (BZ), resulting in 413 k-points in the irreductible wedge of BZ, that ensure the accuracy of the total energy better than $10^{-2}$ mRy. The magnetic disorder has been analysed within disorder local moment (DLM) formalism [17], by treating the binary alloys as pseudoternary Fe$_{1-c}$Pd$_c$ ones, with (x-c) atoms having spin-up state and c atoms being in state with spin down. The DLM configuration with c=0 describes the ferromagnetic (FM) ground state, while that with c=x/2 has been considered as a paramagnetic (PM) state, which shows no resultant magnetic moment. Really, this state is antiferromagnetic (AF), in which the antiparallel alignment of magnetic moments are compensated, miming the PM state.

3. Results

The total energy calculations have been performed on $\gamma$-Fe$_x$Pd$_{100-x}$ with $0 \leq x \leq 80$ and $\alpha$-Fe$_x$Pd$_{100-x}$ with $75 \leq x \leq 100$ alloys in both FM and NM states. The equilibrium values of the lattice parameters have been determined from a third-order polynomial interpolation of the total energy. The computed lattice parameters are in rather good agreement with experimental data [4,5,18], as shown in Fig.1a, for $\gamma$-Fe$_x$Pd$_{100-x}$ alloys. Although the same composition dependence is shown for $\alpha$-Fe$_x$Pd$_{100-x}$ alloys, the experimental values are higher by $\pm 2 \%$. The difference between the two sets of data may be attributed to the LSDA approximation used in the present calculations and the well known underestimation of the equilibrium lattice constants in case of bulk iron alloys. Good agreement between the computed and experimental lattice parameters was shown in Fe$_x$Pt$_{100-x}$ alloys [13].

Fig.1: Computed and experimental [4,5,18] lattice constants determined in $\gamma$-Fe$_x$Pd$_{100-x}$ (a) and $\alpha$-Fe$_x$Pd$_{100-x}$ (b) solid solutions.
The atom resolved spin polarized density of states, DOS, for Fe and Pd in \( \gamma \)-Fe\(_{50}\)Pd\(_{50}\) and \( \alpha \)-Fe\(_{90}\)Pd\(_{10}\) alloys are shown in Fig.2. The iron atoms in fcc solid solutions exhibit a strong ferromagnetism with almost completely filled majority spin sub-bands. A small contribution to DOS from majority spin sub-bands can be shown for iron in bcc type alloys. Similar behaviour was evidenced in Fe-Pt system. Polarizations of Pd4d and Pt5d bands, parallelly oriented to iron moments, are shown. These result from hybridization effects of Fe3d with Pd4d and Pt5d bands, respectively. The splitting of Pd4d and Pt5d bands can be correlated with their short range exchange interactions with the neighbouring Fe atoms. As a result, the Pd4d and Pt5d band polarizations increase with the iron content up to \( x=15 \) and then saturated to values \( \cong 0.34 \mu_B/\text{Pd atom} \) and \( 0.30 \mu_B/\text{Pt atom} \) in fcc solid solutions. In \( \alpha \)-Fe\(_x\)M\(_{100-x}\) alloys, the M=Pd and Pt saturated polarizations are somewhat higher, of \( \cong 0.42 \mu_B/\text{M atom} \). These values agree well with experimental data \cite{19}. The iron magnetic moments increase as Pd or Pt content is higher-Fig.3. The computed composition dependences of the magnetizations in both Fe\(_x\)Pd\(_{100-x}\) and Fe\(_x\)Pt\(_{100-x}\) solid solutions agree well with experimentally determined magnetic moments.

The exchange interactions in both Fe\(_x\)Pd\(_{100-x}\) and Fe\(_x\)Pt\(_{100-x}\) solid solutions were evaluated in the mean field approximation from the differences between the energies of the ferromagnetic and “paramagnetic” DLM states. From these values, Curie temperatures, \( T_c \), were computed. In \( \gamma \)-Fe\(_x\)M\(_{100-x}\) solid solutions, with M=Pd,Pt these show a maximum located at \( x=60 \) mol \%, while the experimentally determined values have the maxima at \( x=55 \) mol \%-Fig.4. The same computational trend of the two sets of values are shown. The differences in the positions of the two maxima may be related with the single site approximation of CPA, used in the present calculations and also by neglecting the short-range order. A certain degree of chemical short-
range order is generally present even in disordered alloys.

The computed and experimentally determined Curie temperatures can be analysed starting from Néel–Slater curve [21]. When plotted $T_c$ values, in Pd$_x$M$_{100-x}$ alloys, as function of distances between iron atoms, $d_{Fe}$, the same type of dependence is shown as predicted by Néel for the evolution of exchange interactions. In a first order approximation, neglecting the contributions of Pd or Pt atoms to the exchange interactions, these will be proportional to $T_c$ values. Thus, according to Néel [21], the Curie temperatures are expected to decrease from a maximum, situated at $d_{Fe}$=2.75 Å both by increasing or decreasing the distances between Fe atoms.

Fig. 3 Composition dependences of the iron and palladium moments as well as of resultant magnetizations in $\alpha$-Fe$_x$Pd$_{100-x}$ (a), $\gamma$-Fe$_x$Pd$_{100-x}$ (b) and resultant magnetizations in Fe$_x$Pt$_{100-x}$ (c). The experimental data are also plotted [2,4-7].

Fig. 4 Composition dependences of the Curie temperatures in $\gamma$-Fe$_x$M$_{100-x}$ M=Pd,Pt solid solutions. The experimental values are also plotted [4,7,20].
As the $d_{Fe}$ values will be smaller than $\approx 2.50 \, \text{Å}$, the presence of negative exchange interactions is expected. Such a behaviour has been observed in $R_2Fe_{17}$ or $R_2Fe_{14}B$ compounds, where $R$ is a rare earth or yttrium [22]. In the present systems the location of the maxima is at $d_{Fe}=2.69 \, \text{Å}$, little smaller value than predicted by Néel [21]. In this model, the diminution of Curie temperatures of Pd-Fe alloys as function of pressures, while keeping saturation magnetization at 4.2 K nearly constant, as experimentally observed [8], can be easily explained. In case of $\alpha$-$Fe_xPd_{100-x}$ with $10 \leq x \leq 15$, the distances between iron neighbouring atoms are situated between 2.52 and 2.539 Å, very close to $d_{Fe}$ values where negative exchange interactions are expected to be present. Small local distortions of the lattices allow an antiferromagnetically coupling at some iron located in sites situated close to $d_{Fe}=2.50 \, \text{Å}$. The above, superposed on basic ferromagnetic ordering and in interaction with the ferromagnetically coupled atoms can change the antiferromagnetic coupling to an helicoidally arrangement, the modulation varying with iron content, the distances between iron atoms, respectively. Really such a behaviour was shown in Lu$_2$Fe$_{17}$ compound [23].

The spontaneous volume magnetostrictions, $\omega$, were determined from the relative volume difference between FM and DLM states [24]. This effect can be shown in $66 \leq x \leq 75$ composition range of Fe$_x$M$_{100-x}$ alloys. In these alloys the paramagnetic DLM minimum energy with a smaller lattice constant (small magnetic moments), is situated slightly above the magnetic solution with a larger lattice constant. When increasing temperature, the local minimum with a small lattice constant can be populated by thermal fluctuations which counteract the usual thermal expansion due to lattice vibrations [25]. Néel [21] attributed the above anomaly to the magnetic energy variations, as function of the volume, the distances between magnetic atoms, respectively. Also showed that magnetostrictions at $T_c$, are proportional to the square of the moments. The computed $\omega$ values as function of the squares of the magnetic moments difference, between the ferromagnetic and DLM states, in Fe$_x$M$_{100-x}$ alloys, are shown in Fig.5. Linear dependences are shown. The computed values are also close to those experimentally determined [6].

![Fig. 5 Magnetostrictions of $\gamma$-Fe$_x$M$_{100-x}$ solid solutions as function of the difference between the squares of the moments in ferromagnetic and paramagnetic DLM states.](image)

The magnetic properties of Fe$_3$Pt, FePt and Fe$_3$Pt [13], as well as of FePd and Fe$_3$Pd ordered compounds were also computed. These described well the experimental values.
4. Conclusions
The total energy calculations on Fe$_x$M$_{100-x}$ with M=Pd, Pt were performed. The determined equilibrium lattice constants describe rather well the experimental data. The composition dependences of the Fe magnetic moments and Pd4d and Pt5d band polarizations were determined. The computed magnetizations per formula unit agree well with experimental values. The composition dependences of the Curie temperatures were analysed according to Néel-Slater curve. In agreement with this curve, the effects of pressure on Tc’s and magnetizations values were explained as well as the presence of an oscillatory spin component, which coexist with ferromagnetic long range order, in alloys with $10 \leq x \leq 15$. The volume magnetostrictions for Fe$_x$M$_{100-x}$ with M=Pd and Pt scale linearly as function of the difference between the square of magnetizations in ferromagnetic and “paramagnetic” DLM states.

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