Magnetocaloric properties of Fe$_{2-x}$T$_x$P ($T$ = Ru and Rh) from electronic structure calculations and magnetization measurements

B Wiendlocha$^1$, J Tobola$^1$, S Kaprzyk$^1$, R Zach$^2$, E K Hlii$^3$ and D Fruchart$^3$

$^1$ Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Cracow, Poland
$^2$ Faculty of Physics, Mathematics and Applied Computer Science, Cracow University of Technology, Podchorazych 1, 30-084 Cracow, Poland
$^3$ Institut Néel, Dépt. MCMF, Groupe IICE, CNRS, BP 166, 38042 Grenoble Cedex 9, France

E-mail: bartekw@fatcat.ftj.agh.edu.pl

Received 22 July 2008, in final form 7 August 2008
Published 30 September 2008
Online at stacks.iop.org/JPhysD/41/205007

Abstract
An analysis of the magnetocaloric properties of pure and substituted Fe$_2$P compounds is made based on KKR-CPA electronic structure calculations and magnetization $M(H, T)$ measurements. The computed electronic densities of states and magnetic moments are used to calculate the values of both the electronic and magnetic entropies, which agree well with the experimental findings. To elucidate the magnetic properties above the Curie temperature, the paramagnetic state behaviours are simulated using the disordered local moments (DLM) concept. The KKR-CPA computations show that in Fe$_2$P, the Fe magnetic moment of the (3f) site disappears in the DLM state, while the moment of the (3g) site is only slightly lowered, in comparison with the low temperature ferromagnetic state.

1. Introduction

Fe$_2$P is a widely studied compound which orders ferromagnetically (FM) down to $T_C \sim 220$ K, correlating two distinct iron sublattices, thus sharing markedly different magnetic moments. The strongest moment ($\sim 2.2 \mu_B$) is found on the Fe(3g) pyramidal site formed by five P neighbours, whereas the Fe(3f) moment of the tetrahedral (3f) site formed by four P neighbours is about four times smaller ($\sim 0.6 \mu_B$). This ferromagnetic-paramagnetic (FM–PM) transition ($T_C$) is accompanied by a very small volume decrease of $\Delta V/V \sim 0.04\%$, without changing the hexagonal symmetry [1]. Here the FM–PM transition is called $T_C$ in many references from the literature, even if it is not exactly a conventional type Curie temperature. Significant magnetocaloric (MC) properties have been reported recently on this type of compound [2]. At 219 K, for a magnetic field ranging from 0 to 1.3 T, the change in magnetic entropy is found to be $\Delta S_m = 2.5$ J kg$^{-1}$ K$^{-1}$, a value close to that observed for Gd (3 J kg$^{-1}$ K$^{-1}$) at 295 K, a metal used as a reference.

In this paper we focus on pure Fe$_2$P and doped Fe$_{2-x}$T$_x$P systems, with $T$ being 4d elements as Ru and Rh. The electronic structure as well as magnetic properties of these compounds are derived from the Korringa–Kohn–Rostoker (KKR) method with the coherent potential approximation (CPA). In the case of the ordered Fe$_2$P compound, the CPA is used to study the paramagnetic state, in the framework of the so-called disordered local moments (DLM) concept [3]. The aim of this work is to determine the MC effect on the one hand and the electronic and magnetic properties on the other. Accordingly, the electronic and magnetic contributions to entropy are calculated, since the entropy jump driven by the application of various external magnetic fields appeared to be relevant parameters, thus characterizing the MC material.
2. Computational details

Electronic structure calculations were performed using the fully charge- and spin-self-consistent KKR method [4, 5]. For pure Fe₂P, the full potential calculations were done, while for disordered systems, the KKR–CPA technique was used within the muffin-tin model of crystal potential. Fe₂P has a hexagonal structure (space group P-62m, No 189) with the low-temperature lattice parameters [1] \( a = 5.866 \, \text{Å}, \; c = 3.456 \, \text{Å} \). In the unit cell, iron atoms occupy tetrahedral (3f) and pyramidal (3g) sites, while phosphorus is located on the (2c) and (1b) sites. It is noted that in the Fe₂P hexagonal type of structure, both the (3f) and (3g) positions approximate rather well a hcp overall metal sublattice. The atomic positions used here are taken from refinements of the neutron diffraction data [6], and the muffin-tin radii of 2.4 a.u. (Fe) and 1.7 a.u. (P) were accounted for. As mentioned above, the CPA approach was also applied to investigate the magnetically disordered system as a model of the paramagnetic state (i.e. the DLM state). Bearing in mind that these computations refer to the ground state properties, without accounting for temperature effects, the DLM computations should reasonably simulate magnetic characteristics above the Curie temperature.

Originally, the KKR–CPA–DLM methodology was applied to study the electronic structure of transition metals in the paramagnetic state [3, 7]. Similarly to the chemical disorder, the magnetic disorder can be seen analogous to that of an \( A_x B_{1-x} \) alloy, where atoms \( A \) and \( B \) keep opposite magnetic moments. In the DLM model, both \( A \) and \( B \) atoms occupy the same crystallographic site, thus for \( x = 0.5 \), the total magnetic moment is zero (if the \( A \) and \( B \) magnetic moments have the same magnitude). In the case of two nonequivalent iron sublattices in Fe₂P, this means that for the 3f site atom \( A \) is for Fe⁺(3f) and atom \( B \) is for Fe⁺(3f) and similarly for the 3g site, Fe⁺(3g) and Fe⁺(3g). The ‘local’ \( \mu_A \) and \( \mu_B \) magnetic moments are non-zero and they are randomly distributed among the crystal sites, as for a ferromagnetic material above \( T_C \). The KKR–CPA calculations of the DLM state are fully self-consistent, i.e. both \( A \) and \( B \) atoms have independent spin-polarized potentials, and consequently the magnetic moments of both atoms are computed independently. As expected, the final magnetic moments in the DLM state are different from those obtained in the ferromagnetic state, since the electronic structure of a magnetically disordered ‘alloy’ is different. Because of the two non-equivalent iron sites occupied in Fe₂P by ‘magnetic’ atoms, the CPA had to be applied simultaneously on tetrahedral and pyramidal sites. For fully converged crystal potentials, total and site-dependent magnetic moments were also calculated. The Fermi level \( (E_F) \) was determined using the generalized Lloyd formula [9].

In order to analyse the MC effect characteristics in the vicinity of the magnetic phase transition, the entropy and its variation were taken into account. The total entropy can be decomposed into the electronic, magnetic and lattice contributions:

\[
S_{\text{tot}} = S_{\text{el}} + S_{\text{m}} + S_{\text{lat}}.
\]  

The electronic entropy as a function of temperature \( T \) can be computed using DOS functions \( n(E) \) and the formula [10]:

\[
S_{\text{el}} = -R \int_{E_{\text{min}}}^{E_{\text{max}}} \frac{d\epsilon n(\epsilon)}{\epsilon} \ln \left[ f(\epsilon) + (1 - f) \ln(1 - f) \right].
\]  

where \( R \) is the gas constant, and \( f \) is the Fermi–Dirac distribution function, \( k_B \) being the Boltzmann constant:

\[
f = f(E, \mu_e, T) = \frac{1}{\exp[(E - \mu_e)/k_B T] + 1}.
\]  

The chemical potential \( (\mu_e) \) is a function of temperature \( T \), and is obtained self-consistently from DOS normalization integral, \( N_{\text{val}} \) being the total number of valence electrons:

\[
N_{\text{val}} = \int_{E_{\text{bottom}}}^{\mu_e} d\epsilon n(\epsilon) f(E, \mu_e, T),
\]  

where integration starts at the bottom of the valence bands. The resulting entropy is given in \( J \, K^{-1} \) per formula unit, when \( n(E) \) is normalized to the number of valence electrons per f.u. (note that the unit cell of Fe₂P contains three formula units).

The electronic entropy weakly depends on the external magnetic field, since, in a first approximation, the application of an external magnetic field only slightly shifts the electronic spectrum. It is noteworthy that Fe₂P exhibits magnetoelastic first-order phase transition at \( T_C \), and both the elastic and magnetic transitions are shifted towards higher temperatures under the external magnetic field. To some extent, this effect allows one to study the impact of a magnetic field on the electronic structure near \( T_C \) by modifying the crystal structure. Thus, we can assume that for temperatures slightly above \( T_C \) the influence of a magnetic field on the electronic DOS is related to the change in the crystal parameters (from PM to FM ones).

The temperature variation of the magnetic entropy \( S_m \) (connected with the magnetic moments degrees of freedom) cannot be easily evaluated from first principles methods, as it would require calculations of magnetic moments variations with temperature. The DLM approach appears to be of interest here, since it may provide information on the variation of the magnetic moments due to magnetic disordering (similarly to the disordered magnetic structure above \( T_C \)). However, the DLM system is completely disordered, which is the case for temperatures far above \( T_C \), where no short-range ordering takes place. Thus the DLM model appears well appropriated to calculate the magnetic entropy, at relatively high temperatures, only.

In order to investigate the magnetic entropy behaviours close to the transition point one can use the magnetic moments computed in the ferromagnetic state, with the temperature effects taken into account within the mean-field approximation. The magnetic entropy of a ferromagnetic system at a temperature \( T \) and in a magnetic field \( H \), is given by [11]:

\[
S_m = R \left[ \ln \left( \frac{2J + 1}{\sinh \left( \frac{2J}{T} \right)} \right) - x B J(x) \right],
\]
where \( B_J(x) \) is the Brillouin function, and
\[
x = \frac{g \mu_B J H}{k_B T} + 3 \frac{T_C}{T} \frac{\mu(T)}{g \mu_B (J + 1)},
\]
where \( \mu(T) \) is the effective magnetic moment of an atom in temperature \( T \), obtained from self-consistent equation \( \mu(T) = \mu(0) B_J(x) \). The \( \mu(0) = g J \) is the zero-temperature saturation magnetic moment (in \( \mu_B \) units), as obtained from the KKR–CPA calculations. This formula gives the well-known maximum saturation entropy \( S_{\text{sat}}^\text{max} = R \ln (2J + 1) \).

For the considered multi-component compounds, the magnetic entropy was calculated independently for each magnetic atom, on the 3f and 3g sites, respectively, and the atomic contributions were added, since the entropy is an intensive parameter. In this work, we intend to discuss the entropy behaviours, as far as possible, without any adjustable parameters, such as those needed for the Bean–Rodbell model, as e.g. to reproduce the MC properties of MnAs [12]. Finally, the experimental ordering temperature \( T_C \) is the only external parameter used in the model. We are aware that the simplified mean-field approach cannot fully represent the complexity of the magnetic properties of systems such as Fe3P, but one should find it valuable when discussing trends in magnetic entropy. It is worth noting that in Fe2P the change in entropy. However, as was earlier mentioned, for Fe2P at the magnetic field, is important, and the magnetic field affects important, since only the change in the total entropy, caused by the field induced PM–FM transition is accompanied because the field induced PM–FM transition is accompanied by an elastic type transition. This behaviour may modify the dynamic properties of the system including the lattice transition. It was deduced [13, 14], that the lattice entropy change along the transition is \( \Delta S_{\text{lat}} \sim -0.06 \text{J} \text{kg}^{-1} \text{K}^{-1} \), to compare with the total change \( \Delta S \sim 1.4 \text{J} \text{kg}^{-1} \text{K}^{-1} \) determined by specific heat measurements in the zero magnetic field. For finite magnetic fields, one can assume that the lattice contribution is not considerably larger.

3. Experimental details

Structural and magnetic investigations were performed for samples with composition Fe1.85Rh0.15P and Fe1.75Rh0.25P. The samples were prepared starting from 99.9% pure elements, mixtures of fine powders were sealed in evacuated silica tubes and then progressively heated up to 850°C for 7 days. A final overheat treatment was realized by using the HF melting technique in a cold crucible in order to melt and then to anneal the samples within the tubes. The quality and crystal structure of the samples were checked by x-ray powder diffraction using a conventional Bragg-Brentano type diffractometer equipped with a backscattering graphite monochromator working at \( \lambda_{\text{Cu}} = 1.7902 \text{Å} \). The magnetic measurements were performed using the BS1 and BS2 extraction type magnetometers developed at the Institut Néel, for high and low temperatures, respectively. From the isothermal magnetization measurements with steps \( \Delta T \) as small as 2 K, the magnetic field varying from 0 to 3 T, the entropy variation was calculated, using the Maxwell–Weiss relation:
\[
\Delta S(H_{\text{max}}) = \int_{0}^{H_{\text{max}}} \left( \frac{\partial M}{\partial T} \right)_H dH.
\]

4. Results and discussion

4.1. Fe3P

The density of states for ferromagnetic Fe3P is presented in figure 1. The lowest lying states are formed from the \( s \)-orbitals of P and the \( s \)- and \( p \)-orbitals of Fe, and more important hybridization of the \( d \)-states of Fe with the \( p \)-states of P builds the conduction bands near the Fermi level. \( E_F \) is located on the decreasing slope of the DOS curve for spin-up electrons, while it is confined in the sharp DOS peak for spin-down electrons, attributed especially to the Fe(3g) site. The high polarization of Fe(3g) \( d \)-DOS results in a large value of magnetic moment 2.33 \( \mu_B \), compared with only 0.50 \( \mu_B \) computed for Fe(3f). The \( p \) atoms possess small negative magnetic moments \(-0.12 \mu_B \) (2c) and \(-0.05 \mu_B \) (1b). The total magnetization per formula unit was found to be as large as \( M_{\text{sat}} = 2.71 \mu_B \). All these magnetic moments values (obtained from full-potential KKR calculations) agree well with the experimental neutron data (2.20 \( \mu_B \) for Fe(3g), 0.60 \( \mu_B \) for Fe(3f)), as well as the previous magnetization measurements \( M_{\text{sat}} = 2.87 \mu_B \) per f.u. [6]. The magnetic moments resulting from the muffin-tin KKR computations are only slightly different with 2.31 \( \mu_B \) for Fe(3g), 0.80 \( \mu_B \) for Fe(3f) and \( M_{\text{sat}} \sim 3.0 \mu_B \).

Figure 2 presents the DOS in the ‘paramagnetic’ DLM state. At first glance we notice a smoothing of the DOS curve with respect to the ferromagnetic state, likely resulting from the magnetic disorder. Identical DOS shapes for both spin directions gives zero magnetization per unit cell, as expected in the DLM state. The most interesting feature of the KKR–CPA–DLM results is related to the vanishing of the local magnetic moment on the Fe(3f) site, since the site-decomposed DOS components ‘up’ and ‘down’ do not show spin-polarization (figure 2). This suggests that for the Fe(3f) sublattice the disappearance of local magnetic moments in the paramagnetic state may be dramatically fast, as the absence of long-range order appears to be sufficient to destroy magnetic polarization.
on this sublattice (even without accounting for temperature effects). On the other hand, the Fe(3g) sublattice still exhibits a strong spin-polarization, and the ‘local’ magnetic moments are only slightly lowered, compared with the FM case. The spin-opposite magnetic moments are \(+2.1 \mu_B\) and \(-2.1 \mu_B\), respectively, giving a total magnetic moment equal to zero per Fe(3g) site. Furthermore, a separation of the total DOS into two energy ranges can be noted, a fact which was not observed in the ferromagnetic state. The lower part of DOS, similarly to the FM state, is formed from the \(s\)-orbitals of phosphorous and the \(s\)-, \(p\)-orbitals of iron, but with a lower contribution of the iron states, since these states are transferred towards higher energies. Surprisingly, the DOS at \(E_F\) in the DLM state is much smaller than that found in the FM one, i.e. \(n(E_F) \approx 45 \text{ Ry}^{-1}/\text{f.u.} \) (DLM) and \(60 \text{ Ry}^{-1}/\text{f.u.} \) (FM). The marked decrease \(n(E_F)\) is related to the decrease in the DOS on the Fe(3g) site, being about 44 \text{ Ry}^{-1} for the FM phase (mainly spin down) versus only 24 \text{ Ry}^{-1} for the DLM phase. Consequently, the DOS decrease determined near the Fermi level leads to an unexpected decrease in the electronic entropy in the disordered phase.

It is worth noting that the situation found here is similar to what we observe for the MnFeP\(_{1-x}\)As\(_x\) series of magnetic material, which have been demonstrated sharing among the most important MC properties [15], furthermore whose structure is directly isotype to the Fe\(_2\)P one [16, 17].
magnetic moments in the DLM state on the pyramidal site (occupied by Mn) remain large (about 3.0 $\mu_B$) while those on the tetrahedral site (occupied by Fe) are lowered twice (from about 1.0 to 0.5 $\mu_B$).

The electronic entropy variation with temperature, calculated using equation (2) (with chemical potential obtained from equation (4)) and applying the FM and DLM DOS, are shown in figure 3, where DLM is plotted only for $T > T_C$.

We can observe a linear increase in the electronic entropy with increasing temperature, leading to a quite noticeable value compared with the magnetic entropy at low temperatures. For $T < 70$ K electronic entropy is even larger than the magnetic one. For $T = T_C$ the electronic entropy contributions are $S^{\text{FM}} = 7.36 J K^{-1} kg^{-1}$ and $S^{\text{DLM}} = 6.55 J K^{-1} kg^{-1}$, which would give the change in the FM–PM transition $\Delta S_{\text{el}} = S^{\text{FM}} - S^{\text{DLM}} = -0.81 J K^{-1} kg^{-1}$, if we assumed that the DOS below and above the magnetic transition corresponds to the FM and DLM states, respectively. However, this value of $S_{\text{el}}$ should be regarded as an upper limit for the electronic entropy change during the transition, since the (DLM) DOS corresponds to temperatures far above $T_C$, and the (FM) DOS is valid at $T = 0$ K. Experimentally, the evolution of DOS with temperature is expected to be much smoother, and thus the electronic entropy change is expected to be smaller. Besides, the small decrease in the unit cell volume at the first-order transition was found to have a negligible impact on the electronic entropy.

The magnetic entropy as a function of temperature and magnetic field, calculated using equation (2) (with chemical potential obtained from equation (4)) and applying the FM and DLM DOS, are shown in figure 3, where DLM is plotted only for $T > T_C$.

4.2. Substituted Fe$_{2-x}$Ru$_x$P

The Fe$_{2-x}$Ru$_x$P compounds, with $T$ being the 4$d$-elements Ru and Rh, were also considered owing to the observed and unexpected increase in Curie temperature from $T_C \sim 220$ K for Fe$_2$P to 240 K for Fe$_{1.85}$Ru$_{0.15}$P and up to 315 K for Fe$_{1.75}$Rh$_{0.25}$P [2,18]. The crystal structures of those compounds, prepared as mentioned above, were determined using x-ray diffraction. In the case of Fe$_{1.85}$Ru$_{0.15}$P a change in the crystal symmetry from hexagonal to orthorhombic (the Co$_2$P-type unit cell) was observed upon Ru substitution [19]. At room temperature the lattice parameters were refined as $a = 5.756$ Å, $b = 3.579$ Å, $c = 6.622$ Å. In the Co$_2$P-type structure, all the atoms are placed in $4c$ ($x$, $\frac{1}{2}$, $z$) sites and the following atomic positions were determined: Fe-tetrahedral (0.1571, $\frac{1}{2}$, 0.4285), Fe-pyramidal (0.0186, $\frac{1}{2}$, 0.8258) and P (0.2569, $\frac{1}{2}$, 0.1113). The Fe$_{2-x}$Ru$_x$P system maintains the hexagonal unit cell at the lowest Ru concentrations, as previously reported [20]. On the other hand, the Fe$_{1.75}$Rh$_{0.25}$P crystallizes in the Fe$_2$P-type unit cell, with the lattice parameters: $a = 5.886$ Å.
-40 -30 -20 -10 0 5 10 15 20 25 concentration x (%) Epyr -E tet (mRy)

Figure 4. Total energy difference per formula unit in ferromagnetic state for Fe$_{2-x}T_x$P alloys, for cases where T is diluted either on pyramidal or tetrahedral site. H- and O-Fe$_{2-x}Ru_x$P refer to the hexagonal (H) and orthorhombic (O) structures, respectively. The pyramidal site preference is observed in all cases.

c = 3.486 Å and atomic positions Fe(3f) (0.264 06, 0, 0), Fe(3g) (0.585 07, 0, $\frac{1}{2}$), P (0, 0, $\frac{1}{2}$) P ($\frac{1}{2}$, $\frac{1}{2}$, 0).

The impact of both the relative electronegativity and the atomic radii of the metals T and $T'$ in the $TT'$P series was determined earlier in terms of ‘selection rules’ based on metal–metal interactions [21]. The largest (smallest) T or $T'$ atom would prefer to occupy the largest (smallest) site, the pyramidal (tetrahedral) one. Conversely, the most (less) electropositive T or $T'$ atom would prefer being coordinated by 5(4) P neighbours, i.e. pyramid versus tetrahedron. Also, if metal–metal interactions decrease, the polytype structures succeed from tetrahedral (T2: SG P4/nmm, Fe$_2$As type) to hexagonal (H3: SG P-62m, Fe$_2$P type) and to orthorhombic (O4: SG Pnma, Co$_2$P type) with a decrease in the unit volume per formula unit ($V_{T2} > V_{H3} > V_{O4}$) [19, 21].

For the intermediate conflicting situation between the relative electronegativity and the metal radii, more or less disordered occupation schemes of both the pyramidal and the tetrahedral sites have been observed.

Since using x-ray diffraction we are not aware (due to the small substitution rate) whether tetrahedral or pyramidal site is preferred when substituting Fe by Rh or Ru, total energy KKR–CPA calculations for both possibilities were undertaken to study the selective substitution. Figure 4 presents the difference in total energies for the cases where the substitution element was entered exclusively on the tetrahedral or the pyramidal sites. The preference for the pyramidal site is clearly observed, being energetically more favourable. Moreover, and in agreement with the ‘selection rules’ recalled here above, the symmetry lowering observed with Ru can be interpreted as trends for more effective site ordering between Fe and Ru. Interestingly, similar KKR–CPA calculations performed for the Fe$_{2-x}Ni_x$P system resulted in the opposite site preference, favouring the tetrahedral (3f) position. This result confirms well the earlier neutron diffraction experiments [22] and also agrees with the so-called selection rules since Ni is a less electropositive element than Fe, and $r_{Fe} > r_{Ni}$. The previous agreement between experimental and theoretical results gives.
us confidence in the site-preference predictions in Fe$_{2-x}$Ru$_x$P and Fe$_{2-x}$Rh$_x$P. Consequently, all results presented below were obtained assuming the pyramidal selective occupation by Ru and Rh.

Figure 5 shows the evolution of magnetic moments in Fe$_{2-x}$T$_x$P with the T concentration, and figure 6 shows the evolution of the corresponding DOSs. Additionally, to have a better insight into the magnetic behaviours of these compounds, the Fe$_{2-x}$Ru$_x$P system both in the hexagonal (correct at low x, denoted as ‘Ru H’) and the orthorhombic (denoted as ‘Ru O’) phases are presented. In the case of Fe$_{2-x}$Ru$_x$P (Ru is isoelectronic to Fe), the transition to the orthorhombic structure strongly affects the DOS shape, being much smoother, compared with the hexagonal one. The large DOS polarization near the Fermi level, which is the characteristic feature of pure Fe$_2$P, practically disappears with Ru substitution. $n(E_F)$ increases (decreases) for spin-up (spin-down) electrons, which leads to a decrease in the total magnetization, as shown in figure 5. The values of magnetic moment of the constituent atoms change slightly in the considered range of content, but first of all, the orthorhombic phase exhibits much lower magnetization, compared with the hexagonal one. For $x = 0.15$ magnetic moments are about $\mu_{Fe(pyr)} = 2.0 \mu_B$, $\mu_{Fe(tet)} = 0.48 \mu_B$ and $\mu_{Ru} = 0.1 \mu_B$, and are lower with respect to the values expected if the system preserved the hexagonal structure upon doping (according to a decrease of the unit cell volume $V_{O4} < V_{H3}$).

In the case of Fe$_{2-x}$Rh$_x$P the smoothing of spin-up DOS with substitution is less noticeable as seen for Fe$_{2-x}$Ru$_x$P, since for $x = 0.15$ we can still observe well pronounced peaks. However, the DOS polarization and then total magnetization also decrease, in spite of the fact that the spin-down DOS is
less modified. Adding one electron more to the system when replacing Fe by Rh does not significantly move the Fermi level towards the DOS valley (higher energy range), which is in contrast to the rigid-band expectations (see figure 6). The total magnetization of Fe$_{2-x}$Rh$_x$P decreases to $M_{tot} = 2.5 \mu_B$ per formula unit for $x = 0.25$, due to the atomic moments: $\mu_{Fe(pyr)} = 2.37 \mu_B$, $\mu_{Fe(tet)} = 0.84 \mu_B$ and $\mu_{Rh} = 0.18 \mu_B$. It is worth noting that in Fe$_{2-x}$Rh$_x$P the local moments on both the Fe sublattices increase slightly upon substitution.

The electronic entropy for $T = T_C$ are: $S_d = 7.36 \text{ J kg}^{-1} \text{ K}^{-1}$ and $S_d = 10.64 \text{ J kg}^{-1} \text{ K}^{-1}$ for Fe$_{1.75}$Rh$_{0.25}$P and Fe$_{1.85}$Ru$_{0.15}$P, respectively. Such a difference presumably results from the smaller DOS at $E_F$ for the Rh case (see figure 6). The decrease in magnetization of these compounds is reflected in their MC properties.

The magnetic entropy changes, obtained from magnetization measurements using the Maxwell–Weiss relation, are shown in figures 7 and 8 for fields up to 3 T. Moreover, the comparison of Fe$_2$P and substituted compounds is presented in figure 3. We can observe that with respect to pure Fe$_2$P, the magnitude of the measured entropy change is about twice smaller ($\Delta H = 1.3 \text{ T}$, i.e. $1.1 \text{ J kg}^{-1} \text{ K}^{-1}$ (Ru substitution) and $0.94 \text{ J kg}^{-1} \text{ K}^{-1}$ (Rh substitution). The calculated magnetic entropy changes, using the mean-field model and KKR–CPA ferromagnetic moments, correctly reproduce the variations determined experimentally. The computations tend to slightly overestimate the entropy jump (for $H = 0–1.3 \text{ T}$, the calculated $\Delta S_m$ are $1.3 \text{ J kg}^{-1} \text{ K}^{-1}$ for the Ru case and $1.2 \text{ J kg}^{-1} \text{ K}^{-1}$ for the Rh case). This is in contrast to the Fe$_2$P compound, where the simulated $\Delta S_m$ is smaller than the measured one. This is probably due to the fact that Fe$_2$P clearly exhibits first order magnetic transition, which gives a sharper change in magnetization (but less temperature extension), and consequently, when entropy is calculated via the Maxwell relation, the larger derivative $\partial M/\partial T$ gives the larger entropy jump. In both considered Fe$_{2-x}$,P alloys the change
in \( M(H, T) \) near \( T_C \) is not so rapid (suggesting second order transition); thus the entropy curves are smoother than those observed for Fe\(_2\)P (see, [2]).

5. Conclusions

We have presented the results of electronic structure calculations for Fe\(_{2-x}\)TxP systems, obtained by the Korringa–Kohn–Rostoker method with the coherent potential approximation (KKR–CPA). To simulate the paramagnetic state of Fe\(_2\)P, the concept of DLM has been successfully applied. We have found that the magnetic moment appearing on Fe(3f) in the ferromagnetic state completely vanishes in the DLM state, while that on Fe(3g) remains only slightly changed.

The evolution of electronic structure, magnetic and MC properties upon substitution of Fe by Ru and Rh has also been studied, both theoretically (KKR–CPA calculations) and experimentally (magnetization measurements). The pyramidal site preference upon substitution was found from the total energy analysis, in fair agreement with selection rules. Both Ru and Rh substituted in Fe\(_2\)P decrease the total magnetization of the compounds, with a stronger effect in the case of \( T = \text{Ru} \). The electronic entropy was calculated as a function of temperature, using the computed KKR–CPA DOSs. The change in magnetic entropy induced by the magnetic field was considered within the mean-field approximation. In spite of the fact that the mean-field model was applied to a complex chemically disordered ferromagnetic system (two magnetically different sublattices), the agreement between the theoretical model and the experimental results was found to be quite satisfactory.

Acknowledgments

This work was partly supported by the Polish Ministry of Science and Higher Education under the grant no. P03 B 113-29 and 44/N-COST/2007/0 as well as the Polish–French collaboration project POLONIUM.