

Microscopic theory of magnetism in the magnetocaloric material $\text{Fe}_2\text{P}_{1-x}\text{T}_x$ ($\text{T} = \text{B}$ and Si)E. K. Delczeg-Czirjak,^{1,*} L. Bergqvist,¹ O. Eriksson,² Z. Gercsi,³ P. Nordblad,⁴ L. Szunyogh,⁵ B. Johansson,^{1,2} and L. Vitos^{1,2,6,†}¹*Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, SE 10044 Stockholm, Sweden*²*Division of Materials Theory, Department of Physics and Astronomy, Uppsala University, Box 516, SE 751210 Uppsala, Sweden*³*Department of Physics, Blackett Laboratory, Imperial College London, London SW7 2AZ, United Kingdom*⁴*Department of Engineering Sciences, Uppsala University, Box 534, SE 75121 Uppsala, Sweden*⁵*Department of Theoretical Physics and Condensed Matter Research Group of the Hungarian Academy of Sciences, Budapest University of Technology and Economics, Budafoki t 8, HU 1111 Budapest, Hungary*⁶*Division of Materials Theory, Research Institute for Solid State Physics and Optics, Wigner Research Center for Physics, P.O. Box 49, HU 1525 Budapest, Hungary*

(Received 23 February 2012; revised manuscript received 11 July 2012; published 20 July 2012)

Landau phenomenological theory in combination with first-principles calculations was used to reveal the origin of the metamagnetic nature and the unusually strong dependence of the ordering temperature with doping of the Fe_2P compound. We show that the magnetism of the two sublattices occupied by Fe atoms has an entwined codependency, which is strongly influenced by alloying. We furthermore demonstrate that a constrained disordered local moment approach combined with Monte Carlo simulations can only reproduce the experimental ordering temperatures in these technologically important prototype alloys for magnetocaloric refrigeration.

DOI: [10.1103/PhysRevB.86.045126](https://doi.org/10.1103/PhysRevB.86.045126)

PACS number(s): 75.30.Sg, 71.20.Be, 75.30.Kz, 75.50.Bb

Magnetic refrigeration techniques have recently been suggested as an alternative for efficient cooling in various applications.¹ In current research efforts to find the most suitable candidates, a large variety of materials has been explored, from first-order magnetostructural transitions with localized magnetic moments to second-order-type transitions with itinerant magnetism.^{2–6} Although materials with first-order-type magnetostructural transitions offer large magnetocaloric effects (MCEs) around room temperature, the accompanying thermal and magnetic hysteresis inhibits their applicability. Metamagnetic transitions based on magnetoelastic interactions caused by the onset of exchange interaction (striction) also provide large MCEs but at a low hysteresis cost.

One of the most feature-rich materials of this kind is CoMnSi , with a pronounced magnetic-field-induced metamagnetism and associated negative MCE due to the giant magnetoelastic coupling within the antiferromagnetic ground state.⁷ Furthermore, a large positive MCE over the itinerant electron metamagnetic transition of $\text{LaFe}_{13-x}\text{Si}_x$ has been widely reported.⁸ This itinerant electron metamagnetic transition is simultaneously followed by an approximately 0.5% increase in volume, without a significant change in the cubic symmetry, and has been ascribed to the multiple energy minima in the total energy versus magnetization profile.⁹

Currently, a competitor for the latter system is represented by the $(\text{Fe,Mn})_2(\text{P,Si,As})$ alloys,² where the magnetoelastic transition of the hexagonal lattice is accompanied by a large MCE. In these rare-earth free alloys the metamagnetic transition temperature of the Fe_2P parent compound (~ 219 K)^{10,11} has been successfully raised to room temperature with the partial replacement of Fe by Mn and P by As or Si.¹²

Prior to the interest in these materials as a magnetic cooling medium, the peculiar magnetoelastic transition of the Fe_2P compound was thoroughly investigated.^{13–15} Yamada and Terao¹⁶ reported that Fe atoms at the tetrahedral $3f$ site show metamagnetic behavior responsible for the first-order transition at T_C . They proposed a model based on Landau-

Ginzburg theory by taking into account the effect of spin fluctuations. The unusually strong dependence of T_C upon doping quantities of the p -block elements of As,¹⁷ Si,¹⁸ or B¹⁹ onto the P site, however, is not understood. For instance, 8 at% of B doubles the magnetic ordering temperature (Table I), allowing fine-tuning of the magnetic transition for cooling applications.

In this article, we use density functional theory combined with the Landau phenomenological model and Monte Carlo (MC) simulations to study comparatively the strong magnetic ordering dependence of the metamagnetic Fe_2P compound with doping by B and Si. We show that small alloying effects lead to locally stabilized ferromagnetism of the otherwise metastable magnetic Fe sublattice. We furthermore demonstrate that collective ferromagnetic (FM) theory would significantly overestimate the Curie temperature, while the theory of a constrained disordered local moment can reasonably explain the remarkable composition dependence of the T_C of these magnetocaloric compounds.

$\text{Fe}_2\text{P}_{1-x}\text{T}_x$ ($x = 0$ when $\text{T} = \text{P}$, $x \leq 15\%$ when $\text{T} = \text{B}$, and $x \leq 25\%$ when $\text{T} = \text{Si}$) crystallizes in a hexagonal crystal structure (space group $P\bar{6}2m$)^{11,18–20} with two types of triple-occupied Fe sites: Fe-I in the tetrahedral- $3f$ positions and Fe-II in the pyramidal- $3g$ positions. Both the volume and the hexagonal axial ratio (c/a) change upon doping the P site (Table I).

The nature of magnetism and the magnetic phase transition have often been discussed via the Landau expansion of the magnetic energy, viz., $E(M) = \frac{1}{2}AM^2 + \frac{1}{4}BM^4 + \frac{1}{6}CM^6$, with $C > 0$. The sufficient condition for an FM ground state at 0 K is $A < 0$ (Stoner criteria). Ferromagnetism appears even for $A > 0$ if $AC/B^2 < 3/16$ and B is large and negative.²¹ Furthermore, the FM solution can be stabilized by an internal (exchange) or by an external (applied) magnetic field, when $3/16 < AC/B^2 < 9/20$.^{21,22} The former is the case for the Fe-I sublattice in Fe_2P , where the FM ordering appears as a result of the exchange field created by the Fe-II atoms.¹⁶ The

TABLE I. Experimental volume (V), c/a ratio, and T_C for Fe_2P ,^{11,20} $\text{Fe}_2\text{P}_{0.9}\text{Si}_{0.1}$,¹⁸ and $\text{Fe}_2\text{P}_{0.92}\text{B}_{0.08}$.¹⁹ The dimensionless quantity κ is reported in the last column (see text for definition).

	V (\AA^3)	c/a	T_C (K)	κ
Fe_2P	103.10	0.589	219	0.263
$\text{Fe}_2\text{P}_{0.9}\text{Si}_{0.1}$	103.92	0.578	370	0.247
$\text{Fe}_2\text{P}_{0.92}\text{B}_{0.08}$	102.14	0.570	450	0.208

metamagnetic behavior of the Fe-I sublattice is reactivated at temperatures close to T_C , when the exchange field of the Fe-II sublattice drops below a critical value.

We investigate the magnetism in Fe_2P and $\text{Fe}_2\text{P}_{1-x}\text{T}_x$ ($T = \text{B}$ and Si) solid solutions by considering the magnetic energy in terms of the chemical composition and local magnetic moments m_1 and m_2 on the Fe-I and Fe-II atoms, respectively (Fig. 1). For each composition, the total energies were calculated as a function of magnetic moments using the exact muffin-tin orbital method.²³ We adopted the local spin density approximation,²⁴ which turned out to give a good description of the magnetic properties of Fe_2P .^{15,16,25} The chemical and magnetic disorder was treated via the coherent potential approximation.²⁶ All calculations were performed for the experimental structures (Table I). The numerical parameters were set so that the total energy was converged within 0.1 mRy/atom.

For all three systems in Fig. 1, the magnetic energy shows a minimum around $m_1 \sim 1$ and $m_2 \sim 2$ and a saddle point around $m_1, m_2 \sim 0$. The local minimum (maximum) in terms of m_1 (m_2) around the latter stationary point indicates a metamagnetic Fe-I (FM Fe-II) sublattice. Since the energy plateau around the saddle point decreases with doping, we envisage that the metastable finite-moment state of the Fe-I site is shifted toward lower energies with doping by B or Si.

In order to shed light on the behavior of the Fe-I sublattice, we separate the magnetic energies originating from the two types of Fe sublattices according to

$$E(m_1, m_2) = \frac{1}{2}a_1m_1^2 + \frac{1}{4}b_1m_1^4 + \frac{1}{6}c_1m_1^6 + \frac{1}{2}a_2m_2^2 + \frac{1}{4}b_2m_2^4 - Jm_1m_2, \quad (1)$$

where the Landau coefficients (a_1 , b_1 , c_1 , a_2 , and b_2) and the exchange interaction between the two magnetic sublattices (J) are obtained by fitting the magnetic energy calculated as a function of $M = m_1 + m_2$, with the constraint $(\frac{\partial E(m_1, m_2)}{\partial (m_1 - m_2)})_M = 0$. Note that invoking higher order terms for m_2 has a negligible influence on the other six parameters. A similar expression was used by Yamada and Terao.¹⁶

According to Eq. (1), the dimensionless quantity $\kappa \equiv a_1c_1/b_1^2$ defines the relative stability of the FM ordering of the Fe-I sublattice, compared to the nonmagnetic state. It is found that Fe_2P has the largest κ (Table I), which means that the finite-moment state of the Fe-I sublattice (when the interaction with the Fe-II site is neglected) is the least stable, compared to that of the doped systems. For $\text{Fe}_2\text{P}_{0.92}\text{B}_{0.08}$, κ is close to the FM limit $3/16$ (0.19), indicating that the stability of the finite-moment state of Fe-I is significantly increased by B doping. For the Si-doped system, κ is in between that of pure and that of B-doped Fe_2P .

For a detailed analysis, we now express the magnetic energy as a function of m_1 , eliminating the FM interaction (Jm_2) of the Fe-II sublattice (according to our calculations J is always positive). The corresponding magnetic energy $E(m_1, m_2 = 0)$ is shown in Fig. 2. This energy has a global minimum at $m_1 = 0$ for all three systems and an inflection point/local minimum at $m_1 \sim 1$ for the pure Fe_2P /doped systems. Hence, in all alloys considered here, the magnetic ordering of the Fe-I sublattice is stabilized by the exchange field created by the Fe-II sublattice.

We propose the following scenario for the magnetic transition in pure and doped Fe_2P systems. When the average magnetic moment of the Fe-II sublattice is sufficiently large, say above a critical value m_2^c , then Jm_2 is strong enough to order the magnetic moments on the Fe-I sublattice. A finite temperature reduces the average moment of the Fe-II site (also the Fe-I site) so that, with increasing temperature, one approaches from above m_2^c . This happens for Fe_2P - as well as for B- or Si-doped compounds. However, according to Fig. 2, in $\text{Fe}_2\text{P}_{0.9}\text{Si}_{0.1}$ and, especially, in $\text{Fe}_2\text{P}_{0.92}\text{B}_{0.08}$ the Fe-I sublattice has a stronger internal tendency to form a finite-moment state compared to Fe_2P . Thus, the value of m_2^c is smaller for B- and Si-doped systems than for Fe_2P . Therefore,

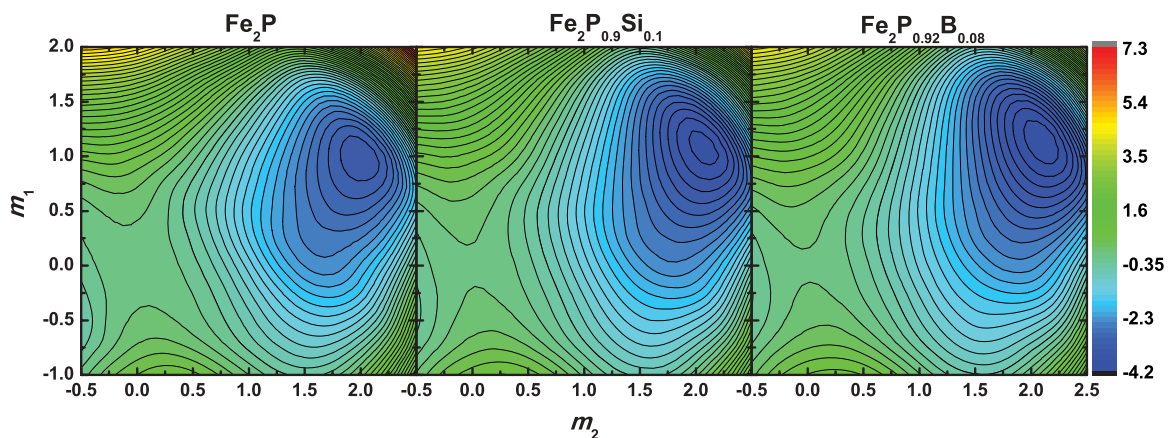


FIG. 1. (Color online) Magnetic energy surface (in units of mRy) for Fe_2P , $\text{Fe}_2\text{P}_{0.9}\text{Si}_{0.1}$, and $\text{Fe}_2\text{P}_{0.92}\text{B}_{0.08}$ calculated as a function of the local magnetic moments at Fe-I (m_1) and Fe-II (m_2) sites. Energies are shown relative to the nonmagnetic value at $m_1 = m_2 = 0$.

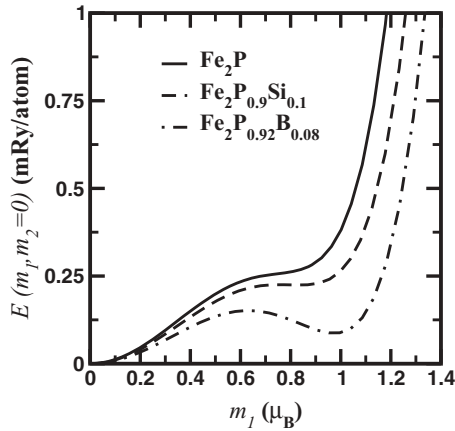


FIG. 2. Magnetic energy [$E(m_1, m_2)$] plotted as a function of m_1 for $m_2 = 0$. Solid line, Fe_2P ; dashed line, $\text{Fe}_2\text{P}_{0.9}\text{Si}_{0.1}$; and dashed-dotted line, $\text{Fe}_2\text{P}_{0.92}\text{B}_{0.08}$.

it should be possible to reach higher ordering temperatures in the alloyed samples compared to the host compound.

Based on the above microscopic picture, one would anticipate that the magnetic exchange interactions calculated for an FM state of Fe_2P -based systems, with an accompanying large moment of the tetrahedrally coordinated Fe atom, do not represent well the state of affairs close to the ordering temperature. This is because fluctuations of the moments on the pyramidally bonded Fe atom diminish the exchange interaction between the magnetic sublattices, which brings forth the metamagnetic behavior of the Fe-I sublattice at (or close to) the ordering temperature. A more consistent approach to this problem is the disordered local moment²⁷ model. Here we adopt a constrained disordered local moment (cDLM) model with a vanishing configurational-averaged total magnetic moment at the Fe-I sites, whereas the disordered local Fe-I moments as well as the FM Fe-II moments were determined fully self-consistently.

With exchange parameters (J_{ij} , with i and j denoting Fe positions) evaluated for both the FM and the above cDLM configurations, we made use of MC simulations to estimate the Curie temperature. Exchange interactions were calculated within the magnetic force theorem.²⁸ Curie temperatures were estimated using MC simulations based on the Metropolis algorithm as implemented in the UppASD program²⁹ in combination with the cumulant crossing method.³⁰

The results of the MC simulations are shown in Fig. 3. It is apparent that the Curie temperature for all alloy concentrations is considerably overestimated by using the exchange coupling constants (J_{ij} values) obtained from the FM configuration.³¹ Moreover, using the FM J_{ij} values, we find that 15% B produces an $\sim 55\%$ increase in T_C , compared to the $\sim 130\%$ increase seen in experiments.^{11,19} The failure of the FM reference state is due to the fact that this state cannot capture the effect of metamagnetic behavior of the Fe-I moment near the transition temperature, which influences the J_{ij} and, in turn, the value of the theoretical T_C . However, a calculation using the cDLM configuration at the Fe-I site reproduces well the behavior of the ordering temperature, both the absolute values and, more importantly, the strongly increasing trend of T_C with respect to doping.

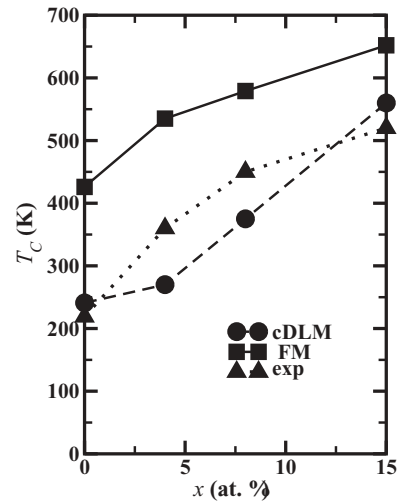


FIG. 3. Theoretical Curie temperatures calculated for FM (squares) and cDLM (circles) states. Experimental data^{11,19} are shown by triangles.

The magnetic properties of the two Fe sites of the Fe_2P -based magnetocaloric materials show a pronounced codependence. Our study demonstrates that this coupling becomes less significant with increasing B or Si substitution at the P site, as a result of lowering the energy of the finite-moment FM state of the Fe-I sublattice with doping. The intricate dependence of the magnetic moment on the Fe-I site and the coupling to the Fe-II site bring about an order-disorder transition of the magnetism that is different compared to that of simple ferromagnets like FM Fe. The escalating temperature causes fluctuations in the Fe-II moment and gradually removes its exchange coupling to the Fe-I moment. With increasing B or Si concentration the Fe-I moment has a greater internal stability and can hence maintain a finite value at higher temperatures. In a bootstrapping scenario, this sustains the exchange coupling between the Fe-I and the Fe-II sites, so that the Fe-I moment survives and the ordering temperature is pushed dramatically to higher temperatures.

The disclosed picture of a delicate and entwined coupling between Fe-II and Fe-I magnetism is consistent with observations of T_C with respect to B and Si doping and provides a crucial microscopic explanation for why Fe_2P -based materials have suitable magnetic properties for magnetocaloric applications. The atomistic approach presented here could be especially valuable in the design of new magnetocaloric materials with a tailored metamagnetic transition around room temperature.

The authors acknowledge support from the Swedish Research Council, the Swedish Energy Agency, the Swedish Foundation for Strategic Research, the European Research Council (Grant Nos. 228074-ALPAM and 247062-ASD), the KAW Foundation, the Swedish Foundation for International Cooperation in Research and Higher Education, the Hungarian Scientific Research Fund (Research Projects OTKA 84078 and K77771-IN83114), the Swedish e-Science Research Centers (SeRC and eSSENCE), STANDUPP, and the Swedish National Infrastructure for Computing (Matter).

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