Magnetocrystalline anisotropy of Fe\textsubscript{5}PB\textsubscript{2} and its alloys with Co and 5\textit{d} elements: a combined first-principles and experimental study

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The Fe\textsubscript{5}PB\textsubscript{2} compound offers tunable magnetic properties via the possibility of various combinations of substitutions on the Fe and P-sites. Here, we present a combined computational and experimental study of the magnetic properties of (Fe\textsubscript{1−\textit{x}}Co\textsubscript{\textit{x}})\textsubscript{5}PB\textsubscript{2}. The calculated magnetic moments, Curie temperatures, and magnetocrystalline anisotropy energies (MAEs) are found to decrease with increasing Co concentration. Co substitution allows for tuning the Curie temperature in a wide range of values, from about six hundred to zero kelvins. As the MAE depends on the electronic structure in the vicinity of Fermi energy, the geometry of the Fermi surface of Fe\textsubscript{5}PB\textsubscript{2} and the \textit{k}-resolved contributions to the MAE are discussed. Low temperature measurements of an effective anisotropy constant for a series of (Fe\textsubscript{1−\textit{x}}Co\textsubscript{\textit{x}})\textsubscript{5}PB\textsubscript{2} samples determined the highest value of 0.94 MJ m\textsuperscript{-3} for the terminal Fe\textsubscript{5}PB\textsubscript{2} composition, which then decreases with increasing Co concentration, thus confirming the computational result that Co substitution reduces the MAE of (Fe\textsubscript{1−\textit{x}}Co\textsubscript{\textit{x}})\textsubscript{5}PB\textsubscript{2}. However, the relativistic version of the fixed spin moment method reveals that a reduction in the magnetic moment of Fe\textsubscript{5}PB\textsubscript{2}, by about 25\%, produces a fourfold increase of the MAE. Furthermore, calculations for (Fe\textsubscript{0.95}X\textsubscript{0.05})\textsubscript{5}PB\textsubscript{2} (X = 5\textit{d} element) indicate that 5\% doping of Fe\textsubscript{5}PB\textsubscript{2} with W or Re should double the MAE. These are results of high interest for, e.g., permanent magnet applications, where a large MAE is crucial.

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I. INTRODUCTION

Many sectors of modern technology depend on magnetic materials, which are used in such ubiquitous applications as electric motors, power generators, transformers, and recording media. Hence, magnetic materials are crucial, not only for the digital technology revolution observed in past decades, but also for the green energy revolution expected within the years to come. The fundamentally and technologically most important intrinsic parameters of magnetic materials include the Curie temperature (\(T_C\)), saturation magnetization (\(M_s\)), and magnetocrystalline anisotropy energy (MAE). These parameters are important in a wide variety of applications, including hard and soft magnetic materials for energy conversion, spintronics, and information storage. Thus, the ability to predict these basic magnetic parameters from first principles is of utmost importance, and accurate modern electronic structure calculations provide an indispensable tool for exploring new materials with desired properties. In parallel, experimental synthesis and characterization retains its fundamental importance and a close interplay between computational and experimental work is of ever increasing value in modern materials discovery.

One example of an area in which the search for new magnetic materials, with specific combinations of properties, has been intense in recent years is that of permanent magnets. In this field it is typically desirable to have large \(M_s\), \(T_C\) and MAE. This combination is obtained in the commonly used rare-earth transition metal compounds, such as NdFe\textsubscript{14}B\textsubscript{2}. However, the so called Rare-Earth Crisis\textsuperscript{1} triggered immense international research initiatives in search for new substitute permanent magnet materials with reduced amounts of, or no, rare-earth elements\textsuperscript{2−6}. The main challenge in this context is obtaining a sufficiently large MAE in transition metal compounds, where a uniaxial (e.g. tetragonal or hexagonal) crystal structure is a crucial prerequisite. Other
areas of applications depend upon other combinations of properties. For example, for magnetocaloric solid state cooling, it is desirable to be able to tune the ordering temperature such that it coincides with the operating temperature (often room temperature)\textsuperscript{7,8}. Various works have shown how strain engineering or alloying can be used to carefully tune the properties of magnetic materials to obtain desired functionality. For example, it was shown that a careful control of strain and alloy concentration allows for a large MAE in bct FeCo alloys\textsuperscript{9-12}. The potential route to FeCo-based permanent magnets offered by that work inspired subsequent studies aiming to stabilize tetragonality in FeCo by B or C-impurities\textsuperscript{13-15}. Also the tetragonal (Fe\textsubscript{1-x}Co\textsubscript{x})\textsubscript{2}B compound has been carefully studied due to its tunable MAE as function of $x$\textsuperscript{16-20}, which, furthermore, has an intriguing temperature dependence\textsuperscript{19,21,22}. It was also shown, in both calculations and experiments, that small substitutions on the Fe/Co site allowed a place of P, for which we have predicted the highest MAE as function of $x$ for isostructural (Fe\textsubscript{1-x}Co\textsubscript{x})\textsubscript{2}P\textsubscript{5} system are our previous results \textsuperscript{22-24}.

The tetragonal family of compounds with compositions (Fe\textsubscript{1-x}Co\textsubscript{x})\textsubscript{5}P\textsubscript{1-y}SiB\textsubscript{2} has also been the subject of numerous recent studies\textsuperscript{23-28}. Additionally, other chemical substitutions, including Mn on the Fe/Co site\textsuperscript{23}, have been considered. Due to the broad range of chemical compositions available, this material offers wide tunability of its magnetic properties. Furthermore, the tetragonal crystal structure could potentially allow for a large MAE and, thus, make the compounds interesting within the context of permanent magnet applications. The materials also exhibit other interesting aspects, such as the temperature dependent spin-reorientation transition in Fe\textsubscript{5}SiB\textsubscript{2}\textsuperscript{25}.

This work focuses on the magnetocrystalline anisotropy of the Fe\textsubscript{5}PB\textsubscript{2} compound and its alloys with Co and 5$d$ elements. Fe\textsubscript{5}PB\textsubscript{2} crystallizes in the Cr\textsubscript{5}B\textsubscript{3}-type structure with a body-centered tetragonal (bct) unit cell, space group 14/mcm\textsuperscript{29} (see Fig. 1).

The unit cell of Fe\textsubscript{5}PB\textsubscript{2} consists of 4 formula units (32 atoms). Fe atoms occupy two inequivalent sites Fe\textsubscript{1} (16\textit{l}) and Fe\textsubscript{2} (4\textit{c}). Fe\textsubscript{1} atoms are distributed on the 16-fold position, Fe\textsubscript{2} and P on the 4-fold, and B on the 8-fold position. Theoretical and experimental crystallographic parameters are presented in Table I.

![FIG. 1. The crystal structure of Fe\textsubscript{5}PB\textsubscript{2}, space group 14/mcm (no. 140).](image-url)

**TABLE I.** The optimized crystallographic parameters for Fe\textsubscript{5}PB\textsubscript{2} and Co\textsubscript{5}PB\textsubscript{2} as calculated with the FPL014-GGA. Space group 14/mcm, no. 140. The Wyckoff positions are: Fe\textsubscript{1}/Co\textsubscript{1} (x, x+1/2, z), Fe\textsubscript{2}/Co\textsubscript{2} (0, 0, 0), P (0, 0, 1/4), and B (x, x+1/2, 0). For comparison the values measured in this work at room temperature for Fe\textsubscript{5}PB\textsubscript{2} and the literature values for Co\textsubscript{5}PB\textsubscript{2} are also reported.

| system            | a [Å] | c [Å] | $x_{Fe_1/Co_1}$ | $z_{Fe_1/Co_1}$ | $x_B$ |
|-------------------|-------|-------|-----------------|-----------------|-------|
| Fe\textsubscript{5}PB\textsubscript{2} (GGA) | 5.436 | 10.296| 0.170           | 0.139           | 0.381 |
| Fe\textsubscript{5}PB\textsubscript{2} (expt.) | 5.492 | 10.365| 0.170           | 0.141           | 0.381 |
| Co\textsubscript{5}PB\textsubscript{2} (GGA) | 5.284 | 10.541| 0.169           | 0.142           | 0.376 |
| Co\textsubscript{5}PB\textsubscript{2} (expt.) | 5.42 | 10.20 | -               | -               | -     |

One of the motivations to investigate the (Fe\textsubscript{1-x}Co\textsubscript{x})\textsubscript{5}PB\textsubscript{2} system are our previous results for isostructural (Fe\textsubscript{1-x}Co\textsubscript{x})\textsubscript{5}SiB\textsubscript{2} system (with Si in place of P), for which we have predicted the highest MAE = 1.16 MJ m\textsuperscript{-3} for Co concentration $x = 0.3$.\textsuperscript{24} Next, the (Fe\textsubscript{0.8}Co\textsubscript{0.2})\textsubscript{5}PB\textsubscript{2} sample (with Co concentration $x = 0.2$) was synthesized by McGuire and Parker\textsuperscript{23} and their magnetic measurements showed an increase of the anisotropy field after Co substitution, which supports our prediction. All the previous experimental studies conducted on the (Fe\textsubscript{1-x}Co\textsubscript{x})\textsubscript{5}SiB\textsubscript{2} system are limited to the Fe-rich compositions, while CoSiB\textsubscript{2} is not known to form.\textsuperscript{23} For melt-spin samples Fe\textsubscript{5}(Si\textsubscript{0.75}Ge\textsubscript{0.25})B\textsubscript{2} Lejeune et al. were determined a relatively high anisotropy constant $K_1$ of about 0.5 MJ m\textsuperscript{-3} at room temperature, which is about double the value for FeSiB\textsubscript{2}\textsuperscript{24,30}. Recently, we also presented a combined experimental and theoretical study of the Fe\textsubscript{5}Si\textsubscript{1-x}P\textsubscript{x}B\textsubscript{2} system, which showed the highest anisotropy constant for the terminal Fe\textsubscript{5}PB\textsubscript{2} composition\textsuperscript{27}.

Fe\textsubscript{5}PB\textsubscript{2} has high $T_C$ of about 655±2 K, magnetic moment of 1.72 $\mu_B$/Fe atom (8.60 $\mu_B$/f.u.), and anisotropy constant $K_1$ of 0.50 MJ m\textsuperscript{-3} measured at 2 K for single crystal.\textsuperscript{26} The value of an effective anisotropy constant $K_{\text{eff}}$ of Fe\textsubscript{5}PB\textsubscript{2} obtained in our previous work is however significantly higher and equal to $\sim 0.9$ MJ m\textsuperscript{-3} at 10 K.\textsuperscript{27} An important parameter, in context of permanent magnets, is magnetic hardness, defined as:

$$\kappa = \sqrt{\frac{|K|}{\mu_0 M_S^2}},$$

where $K$ is the magnetic anisotropy constant and $M_S$ is the saturation magnetization. An empirical rule $\kappa > 1$ specifies whether the material have a chance to resist self-demagnetization.\textsuperscript{4} From the experimental values of $K_{\text{eff}} \sim 0.65$ MJ m\textsuperscript{-3} and $M_S = 0.87$ MA/m\textsuperscript{27}, we determined for Fe\textsubscript{5}PB\textsubscript{2} $\kappa = 0.69$ (at 300 K). It implies, that
without a further engineering of the anisotropy constant, Fe₅PB₂ will stay in a category of semi-hard magnets.⁴

In this work we consider alloying of Fe₅PB₂ with Co and 5d elements. In our recent study of (Fe₁₋ₓCoₓ)₅PB₂ alloys we observed a reduction in magnetization and Curie temperature with an increase of Co concentration.²⁸ McGuire and Parker also found that 20% Co alloying in (Fe₁₋ₓCoₓ)₅PB₂ leads to decrease in magnetization, Curie temperature and anisotropy field.²³ Previously we showed also that increase of the MAE of 3d alloys can be achieved through doping with 5d elements.¹⁹ In this work we follow this idea and calculate the resultant MAEs of Fe₅PB₂-based alloys with 5% substitutions of each 5d element in place of Fe.

II. COMPUTATIONAL AND EXPERIMENTAL DETAILS

A. Computational Details

The electronic band structure calculations for (Fe₁₋ₓCoₓ)₅PB₂ and (Fe₀.₉₅X₀.₀₅)₅PB₂ (X = 5d element) systems were carried out with use of the full-potential local-orbital minimum-basis scheme FPLO14.0-49.³¹ The FPLO was an optimal choice for the accurate calculations of MAE due to the full potential and fully relativistic character of the code. To model the Co and 5d alloying we used the supercell method. The generalized gradient approximation (GGA) was used in the Perdew-Burke-Ernzerhof form (PBE).³² A 16 × 16 × 16 k-mesh was found to lead to well converged results of the MAE. For k-point integration, the tetrahedron method was used.³³ The energy and charge density convergence criteria of ~ 10⁻⁷ eV and 10⁻⁶, respectively, were applied simultaneously. The lattice parameters and Wyckoff positions were optimized for Fe₅PB₂ and Co₅PB₂ within a spin-polarized scalar-relativistic approach. The crystallographic parameters for compositions with intermediate Co concentrations were taken from calculations of full lattice relaxation carried out previously in virtual crystal approximation.²⁸ For the (Fe₀.₉₅X₀.₀₅)₅PB₂ supercells we used the same crystallographic parameters as for the Fe₅PB₂. The MAE was evaluated as a difference between the fully relativistic total energies calculated for quantization axes [100] and [001]. In the adopted sign convention the positive sign of MAE corresponds to an easy magnetization axis along the [001] direction. The Fermi surface (FS) of Fe₅PB₂ was calculated on a 28³ k-mesh in a boundary of the first Brillouin zone. Using the fully relativistic fixed spin moment (FSM) scheme we study the MAE as a function of total magnetic moment (m) for Fe₅PB₂. A supercell method was used to model the chemical disorder.¹⁸,³⁵ To build a supercell, multiplication of the basal unit cell and replacement of an appropriate amount of atoms of one type by atoms of the other type were made. The Fe atoms were replaced by Co or 5d atoms forming the (Fe₁₋ₓCoₓ)₅PB₂ and (Fe₀.₉₅X₀.₀₅)₅PB₂ compositions (X = 5d element). For (Fe₁₋ₓCoₓ)₅PB₂ the considered intermediate compositions were: x = 0.2, 0.4, 0.6, and 0.8. The MAE calculations based on the supercell method are uncommon, as they are time-consuming even for relatively simple alloys. The reason for that is significant increase in the number of inequivalent atomic positions generated for the supercell model. It limits the size of supercells which we can use for MAE calculations. Hence, we study only the supercells including symmetry operations and consisting of up to 16 inequivalent atoms. The considered crystal structures are presented in Fig. 2. Three configurations were considered for Fe₄Co₁PB₂ and Fe₃Co₄PB₂ and one for Fe₃Co₂PB₂ and Fe₂Co₃PB₂ compositions. For the considered supercell models, the energy convergence with a number of k-points was carefully tested. The supercell method was also employed to calculate the MAE of (Fe₀.₉₅X₀.₀₅)₅PB₂ compositions with various 5d elements X. To construct the models, one of twenty Fe atoms in the basal Fe₅PB₂ supercell was replaced by the dopant. It led to the crystal structures containing 10 inequivalent atomic positions. For calculations of the systems with 5d dopants a relatively dense 20 × 20 × 10 k-mesh was used, in order to get the well converged results of MAE.

To compute the Curie temperatures within the mean-field theory (TC^MFT) for the whole series of (Fe₁₋ₓCoₓ)₅PB₂ compositions the FPLO5.00 version of the code was used.³⁶ The TC^MFT is proportional to the total energy difference between the ferromagnetic and para-
magnetic configurations\textsuperscript{37–39} according to:
\[
k_B T_C^{\text{MFT}} = \frac{2}{3} \frac{E_{\text{DLM}} - E_{\text{FM}}}{c},
\]

where \(E_{\text{DLM}}\) and \(E_{\text{FM}}\) are total energies for the paramagnetic and ferromagnetic configurations, \(k_B\) is Boltzmann constant, and \(c\) is total concentration of magnetic atoms. In case of Fe\(_5\)PB\(_2\) containing five Fe atoms (considered as magnetic ones) within a formula unit consisting of eight atoms, the concentration parameter \(c\) is equal \(5/8\). To model the paramagnetic state the disordered local moment (DLM) method was used,\textsuperscript{40} in which the thermal disorder among the magnetic moments is modeled by using the coherent potential approximation (CPA).\textsuperscript{41} The FPLO5 is the latest public version of the code allowing for the CPA calculations and does not have implemented the GGA. Thus, the local density approximation (PW92)\textsuperscript{42} form of the exchange-correlation potential had to be chosen. For the calculations within FPLO5, a scalar-relativistic mode and a \(12 \times 12 \times 12\) \(k\)-mesh were used. In the FPLO5 the magnetically ordered state (resulting in \(E_{\text{FM}}\)) was artificially modeled within the CPA, to avoid numerical discrepancies between the ordered (in principle non-CPA) and DLM (CPA) models. The VESTA code was used for visualization of crystal structure.\textsuperscript{43}

### B. Experimental Details

The samples in the series (Fe\(_{1-x}\)Co\(_x\))\(_5\)PB\(_2\) \((x \text{ from 0.0 to 0.7})\) were synthesized using stoichiometric amounts of the master alloys Fe\(_5\)PB\(_2\) and Co\(_5\)PB\(_2\). The master alloys were prepared, in accordance with previous studies\textsuperscript{27}, from pure elements of iron (Leico Industries, purity 99.995\%), surface oxides reduced in H\(_2\)-gas), cobalt (Johnson Matthey, purity 99.999\%), phosphorus (Cerac, purity 99.999\%), and boron (Wacher-Chemie, purity 99.995\%). This was done by forming first the TM\(_2\)B (TM = Fe, Co), using a conventional arc furnace, and subsequently dropping the phosphorus in a melt of the metal boride in an induction furnace using the drop synthesis method.\textsuperscript{44} All samples were subsequently crushed, pressed into pellets, and heat treated in evacuated silica ampules at 1273 K for 14 days after which they were quenched in cold water. At \(x\) higher than 0.7 the correct crystalline phase could not be produced, all attempts resulted in a decomposition to other crystalline phases. Similar problems with synthesis of Co-rich alloys with negative magnetic anisotropy constant were previously encountered by other experimental groups.\textsuperscript{19,21}

To study the phase content and to perform crystal structure analysis of all samples, a powder X-ray diffraction (XRD) was used. The measurements were done using a Bruker D8 diffractometer equipped with a LynxEye position sensitive detector (4° opening) using CuK\(_{\alpha 1}\) radiation (\(\lambda = 1.540598\ \text{Å}\)) at 298 K in a 2\(\theta\) range of 20°–90°. The crystal structures were evaluated with the software FullProf\textsuperscript{45} using refinements according to the Rietveld method.\textsuperscript{46} The unit cell parameters were precisely studied using the least square refinements of the peak positions, employing the software UnitCell.\textsuperscript{47}

The synthesized samples were magnetically studied using a Quantum Design PPMS 6000. Samples were immobilized in gelatin capsules with varnish. The magnetization at 3 K was measured between applied magnetic fields of 0 and 7.2 MA m\(^{-1}\). The magnetization in SI units was calculated from magnetic moment using the sample weight and the crystallographic volume obtained from the XRD measurements at 298 K. When approaching magnetic saturation the magnetization process is described by the law of approach to saturation (LAS).\textsuperscript{48} LAS has been formulated in several ways\textsuperscript{48–51}, but it takes a general form

\[
\frac{M}{M_S} = \sum_j a_j H^j,
\]

where \(j\) is usually an integer, \(a_j\) are coefficients, \(M\) and \(M_S\) are magnetization and saturation magnetization, and \(H\) is the applied magnetic field. The LAS was used to determine an effective anisotropy constant \(|K_{\text{eff}}|\) in the same implementation as we used before.\textsuperscript{25,27} The interval 93%–98% of the magnetic saturation was used. The applied formula was

\[
\frac{M}{M_S} = 1 + aH + \frac{b}{H} + \frac{c}{H^2}.
\]

The experimental data was fit with four models in which \(a\) and \(b\) coefficients can be zero or non-zero and since \(\frac{1}{H^2}\) term is used to extract \(|K_{\text{eff}}|\) this part is always considered as non-zero. \(|K_{\text{eff}}|\) is given here by

\[
|K_{\text{eff}}| = \sqrt{\frac{15c}{4}} \mu_0 M_S.
\]

The difference in results between all four models are relatively small (max. 0.20 MJ m\(^{-3}\)), thus in the experimental section we present only the \(|K_{\text{eff}}|\) for the simplest model with the coefficients \(a = b = 0\).

### III. RESULTS AND DISCUSSION

The results of first-principles calculations of technologically important magnetic parameters for the considered systems are shown. For (Fe\(_{1-x}\)Co\(_x\))\(_5\)PB\(_2\) the \(M_S, T_C,\) and MAE are presented. For (Fe\(_{0.95}\)X\(_{0.05}\))\(_5\)PB\(_2\) \((X = 5d\) element) the results are limited to MAE and partial magnetic moments. For the main phase – Fe\(_5\)PB\(_2\) – a detailed analysis of electronic structure, magnetic moments, Fermi surface, and MAE is given. The theoretical efforts are complemented by experimental synthesis and measurements of the considered (Fe\(_{1-x}\)Co\(_x\))\(_5\)PB\(_2\) compositions.
A. Electronic Structure of Fe₅PB₂ and Co₅PB₂

The optimized crystallographic parameters of Fe₅PB₂ and Co₅PB₂ are compared in Table I with the results of measurements. For Fe₅PB₂ the agreement between the GGA and experiment is good and for the Co₅PB₂ the GGA underestimates $a$ and overestimates $c$. The disagreement may originate from both theory and experiment. The lattice parameters of Co₅PB₂ were last refined by Rundqvist back in 1962. Unfortunately, we did not manage to synthesize the Co₅PB₂ sample. Furthermore, the limitations of LDA/GGA for modeling Co compounds are recognized. For example, the predicted lattice constant of YCo₂ is underestimated even beyond the general overbinding nature of the LDA.²⁵

![DOS plots for Fe₅PB₂ and Co₅PB₂](image)

FIG. 3. The spin projected partial and total densities of states (DOS) for Fe₅PB₂ and Co₅PB₂. Calculations were done within the FPLO14 PBE+so method.

The spin projected partial and total densities of states (DOS) for Fe₅PB₂ and Co₅PB₂ are presented in Fig. 3. The valence bands of these two metallic systems start around -9 eV. In a range from -9 to -3 eV the main contributions to a valence band come from the P 3p and B 2p orbitals, while from -5 eV up to above $E_F$ the dominant role play the 3d orbitals. The observed spin splitting (proportional to the magnetic moment) is bigger for Fe₅PB₂ than for Co₅PB₂, which is related to a higher filling of the valence band for Co₅PB₂ than for Fe₅PB₂. The majority spin channels of the two compounds are similar and nearly completely occupied. The additional electrons in the Co₅PB₂ fill mainly the minority spin channel, reducing the magnetic moment. The weak spin polarization of the P 3p and B 2p orbitals is induced by the 3d orbitals. The calculated spin polarization on the Fermi level is about 0.46 for Fe₅PB₂ and 0.60 for Co₅PB₂. The spin polarization on the Fermi level is defined as $P = \frac{D_u - D_d}{D_u + D_d}$, where $D_u$ is the density of states at the Fermi level of the majority spin channel, and $D_d$ for the minority spin channel.

B. Magnetic Moments of $(\text{Fe}_{1-x}\text{Co}_x)₅\text{PB}_2$

![Magnetic moment graph](image)

FIG. 4. The Co concentration dependence of total magnetic moment for the $(\text{Fe}_{1-x}\text{Co}_x)₅\text{PB}_2$ system. The results calculated with FPLO14-GGA+so supercell method are denoted by red circles, the results measured at 3 K by blue squares. Linear fits are drawn for a better perception.

The Co concentration dependence of the total magnetic moment ($m_S + m_L$) for the $(\text{Fe}_{1-x}\text{Co}_x)₅\text{PB}_2$ system is presented in Fig. 4, together with the low temperature experimental results. The calculated and experimental $m(x)$ plots are both linear. It means that $m$ for intermediate compositions is an average of contributions from terminal phases Fe₅PB₂ and Co₅PB₂. Extrapolation of the straight line on which the experimental data is arranged suggests a non-zero, but low $m$ for Co₅PB₂. An overestimation of the GGA results in respect to measured $m$ is related to a well know underbinding nature of the GGA. The corresponding $m(x)$ plots based on the virtual crystal approximation and coherent potential approximation can be found in our previous work.²⁸

The calculated spin, orbital, and total magnetic moments ($m_s$, $m_1$, $m$) for Fe₅PB₂ and Co₅PB₂ are collected in Table II. The calculated total magnetic moment of the Fe₅PB₂ equal to 8.85 $\mu_B$/f.u. (1.77 $\mu_B$/Fe atom) is in good agreement with low temperature measurements (2 K) for a single crystal equal to 8.6 $\mu_B$/f.u. (1.72 $\mu_B$/Fe atom).²⁶ For Fe₅PB₂ the calculated magnetic moments on Fe₁ and Fe₂ sites are equal to 1.81 (1.62) and 2.16 (2.16) $\mu_B$, respectively. In parentheses are given estimates from the magnetic hyperfine fields.⁵³ The calculated $m$ of Co₅PB₂, equal to 2.20 $\mu_B$/f.u. (0.44 $\mu_B$/Co atom), is much lower than the value for Fe₅PB₂. Similar values of $m$ on Co for $(\text{Fe}_{1-x}\text{Co}_x)₅\text{PB}_2$ alloys were calculated within the CPA-LDA.²⁸ For comparison, the experimental magnetic moment of hcp Co equal to 1.67 $\mu_B$.⁵⁴ Comparison of total energies between the magnetically ordered and disordered (DLM)⁵⁷ states for Co₅PB₂ showed
TABLE II. The spin, orbital, and total magnetic moments ($\mu_B$ (atom or f.u.))$^{-1}$ for Fe$_5$PB$_2$ and Co$_5$PB$_2$ as calculated with the fully relativistic FPLO-GGA method along the quantization axis [001] (easy axis). The saturation magnetization $M_S$ (MA m$^{-1}$) is evaluated based on the total magnetic moments $m$ and theoretical lattice parameters.

| Site       | Fe$_5$PB$_2$ | Co$_5$PB$_2$ |
|------------|--------------|--------------|
| m$_s$      | 1.78 0.033   | 0.41 0.011   |
| m$_i$      | 2.11 0.052   | 0.64 0.013   |
| P          | -0.13 0.002  | -0.02 0.001  |
| B          | -0.21 0.001  | -0.05 0.000  |
| m          | 8.85 2.20    |              |
| $M_S$      | 1.07 0.28    |              |

a preference for the ordered (ferromagnetic) solution. McGuire and Parker$^{23}$ suggested, however, absence of magnetic ordering for Co$_5$PB$_2$. Concluding, the magnetic ground state of Co$_5$PB$_2$ cannot be unambiguously resolved. In order to solve this problem, the X-ray or electron magnetic circular dichroism (XMCD or EMCD) measurements could be made.

The total magnetic moments of Fe$_5$PB$_2$ and Co$_5$PB$_2$ are almost entirely of spin character, where the 3d orbital magnetic moments ($m_L$'s) are nearly quenched. The $m_L$'s of Fe$_1$ and Fe$_2$ of the Fe$_5$PB$_2$ (calculated for the [001] quantization axis) are equal to 0.033 $\mu_B$ and 0.052 $\mu_B$, respectively. These values surround the $m_L$ value calculated for bcc Fe (0.043 $\mu_B$) and moreover are reduced in comparison to the experimental value for the bcc Fe (0.086 $\mu_B$).$^{55}$ The $m_L$'s of Co$_1$ and Co$_2$ of the Co$_5$PB$_2$ are equal to 0.011 $\mu_B$ and 0.013 $\mu_B$, respectively, and are one order of magnitude smaller than the $m_L$ measured for hcp Co (0.13 $\mu_B$).$^{56}$ Finally, almost no orbital contributions are observed from P and B atoms ($m_L \sim 10^{-3} \mu_B$).

C. Curie Temperature of (Fe$_{1-x}$Co$_x$)$_5$PB$_2$

The Curie temperatures calculated within the mean-field theory ($T_C^{\mathrm{MFT}}$) for the whole concentration range of (Fe$_{1-x}$Co$_x$)$_5$PB$_2$ system are presented in Fig. 5. The corresponding experimental results can be found in our recent work.$^{28}$ The calculated $T_C^{\mathrm{MFT}}$ of Fe$_5$PB$_2$, equal to 547 K, underestimates the experimental values (655±2 K$^{26}$, 640 K$^{23}$, 622 K$^{28}$, and 615 K$^{27}$). An underestimation of $T_C^{\mathrm{MFT}}(x)$ for Fe-rich region is related with an underestimation of the magnetic moments obtained within the LDA. MFT underestimates also the results of more accurate Monte Carlo calculations.$^{27}$ A better agreement with experiment is expected for the results from GGA, however, with the FPLO5-CPA code we are limited to the LDA. The observed overall decrease of calculated $T_C^{\mathrm{MFT}}$ with increase of Co concentration in (Fe$_{1-x}$Co$_x$)$_5$PB$_2$ system stays in agreement with experimental observations.$^{23,28}$ A relatively small

$T_C^{\mathrm{MFT}} = 37$ K predicted for Co$_5$PB$_2$ indicates an ordered magnetic ground state. Linear fit of experimental magnetic moments also suggest non-zero value for Co$_5$PB$_2$. However, other experiment suggests absence of ferromagnetism in Co$_5$PB$_2$. On contrary to the Fe-rich region, the magnetic moments on Co-rich region are most probably overestimated. It is a common failure of the LDA/GGA, which in principle can be overcome with the use of dynamical mean field theory (DMFT).$^{19}$ Taking into account (1) the problems with synthesis of the Co$_5$PB$_2$ phase, (2) preliminary character of the measurements reported by McGuire and Parker, (3) mentioned issues with optimization of the structural model, and (4) limitations of LDA/GGA in modeling magnetic moments of Co-rich phases, we conclude that the Co$_5$PB$_2$ magnetic ground state remains without a definite answer.

The effect on $T_C^{\mathrm{MFT}}$ coming from underestimation of the magnetic moments in LDA can be corrected by taking into account the moments from GGA. In Heisenberg model, $T_C^{\mathrm{MFT}}$ is proportional to squared effective moment ($m_{\text{eff}}^2$). Defining $b = \frac{m_{\text{GGA}}^{\text{GGA}}}{m_{\text{LDA}}}$ the corrected Curie temperature is $b^2T_C^{\text{MFT}}(\text{LDA})$. In case of (Fe$_{1-x}$Co$_x$)$_5$PB$_2$ $b$ is about 1.2. Figure 5 shows that the $b^2T_C^{\text{MFT}}(\text{LDA})$ plot is in very good agreement with experiment.

D. Fermi Surface of Fe$_5$PB$_2$

Figure 6 presents the calculated Fermi surface (FS) of Fe$_5$PB$_2$ in a boundary of the first Brillouin zone. The FS of Fe$_5$PB$_2$ reflects the tetragonal symmetry of the crystal. The FS consists of nine sheets and is relatively complex. The states at the Fermi level ($E_F$) have a Fe 3d character, as can be read from the DOS plots in Fig. 3. The observed FS sheets can be divided into two groups.
Because the band structure was calculated with In Fig. 6, along the orthogonal from the formula: The well known \( \text{orbits.} \)

\[ (a) \text{ we show a cross-section of the } \]

\[ 60 \]

\[ (i), \text{ take the form of pockets enabling only for closed FS } \]

\[ \text{symmetry axis, the remaining sheets, (a)–(b) and (g)–(i), take the form of pockets enabling only for closed FS } \]

\[ \text{orbits.} \]

\[ \text{Because the band structure was calculated with spin-orbit coupling, the FS sheets cannot be unambiguously attributed to a particular spin channel.} \]

The first group consists of four nested sheets of hole-type, see panels (a)–(d) of Fig. 6, and the second group includes the remaining five sheets of electron-type nested in a multiwalled way around the high symmetry point \( Z \), see panels (e)–(i) of Fig. 6. While the sheets (c)–(f) form rather tubular shapes, allowing for open orbits along the symmetry axis, the remaining sheets, (a)–(b) and (g)–(i), take the form of pockets enabling only for closed FS orbits. \(^{57}\) Because the band structure was calculated with spin-orbit coupling, the FS sheets cannot be unambiguously attributed to a particular spin channel.

### E. Magnetocrystalline Anisotropy of \( \text{Fe}_5\text{PB}_2 \)

The results of investigating the MAE of \( \text{Fe}_5\text{PB}_2 \) carried out in this work are: the band structure in vicinity of the Fermi level, one- and two-dimensional \( \text{k} \)-resolved MAE plots, and the cross-section of FS. Our inquiry is complemented by considerations of MAE engineering, as for example reduction of total magnetic moment. The calculated MAE of the \( \text{Fe}_5\text{PB}_2 \) is 0.52 MJ m\(^{-3}\). It indicates a uniaxial magnetocrystalline anisotropy with an easy axis along the tetragonal axis. This result stays in a good agreement with the experimental value of anisotropy constant 0.50 MJ m\(^{-3}\) measured at 2 K and with the previous theoretical findings 0.46 MJ m\(^{-3}\). \(^{26}\) The well known origin of the magnetocrystalline anisotropy is the spin-orbit coupling, which is taken into account in the fully relativistic full potential calculations. In comparison with scalar relativistic approach, the fully relativistic one results in additional splitting of the electronic bands. Since the spin-orbit coupling constant of 3\(d\)-metals is of the order of 0.05 eV, the spin-orbit splitting also does not exceed this value. The spin-orbit splitting leads to slightly different band structures for different quantization axes (e.g. for the orthogonal [001] and [100] axes). Figure 7 presents the band structures calculated for \( \text{Fe}_5\text{PB}_2 \) in the proximity of \( E_F \), together with the MAE contributions per \( \text{k} \)-point obtained with the magnetic force theorem \(^{58-60} \) from the formula:

\[
\text{MAE} = E(\theta = 90^\circ) - E(\theta = 0^\circ) = \\
\sum_{\text{occ}} \epsilon_i(\theta = 90^\circ) - \sum_{\text{occ}} \epsilon_i(\theta = 0^\circ), \quad (6)
\]

where \( \theta \) is an angle between the magnetization direction and the \( c \) axis, \( E(\theta) \) is a total energy for a specific direction; and \( \epsilon_i \) is the band energy of the \( i \)-th state. The spin-orbit splitting is most easily observed for the energy window of a tenth eV around \( E_F \). The \( \text{k} \)-point resolved MAE takes positive and negative values, depending on the spin and orbital character of the bands near the Fermi energy. Generally, negative MAE-contributions coincide with occupied bands for a [100] spin quantization axis (solid red line) being pushed below corresponding bands for a [001] spin quantization axis (dashed blue line), and vice versa for positive contributions. For example, at the \( Z \)-point, there is a negative MAE contribution and at approximately -0.3 eV one can observe a solid red line below the dashed blue line. A more detailed analysis of the MAE contributions is in principle straightforward but somewhat complicated due to the complex band structure. Nevertheless, one can clearly observe the characteristic jumps where the bands cross \( E_F \), confirming the usual behavior that the MAE is determined by the electronic structure around the Fermi energy. Thus, controlling the MAE around \( E_F \) also allows for control of the MAE, as is practically possible, for example, via alloying.

The same form of presentation of the \( \text{k} \)-resolved MAE, as we have shown in Fig. 7, dominates in literature. However, it is possible to plot the MAE(\( \text{k} \)) data within a three dimensional Brillouin zone, similar like the FS. Recently, the 3D MAE(\( \text{k} \)) maps were presented for \( \text{(Fe}_{1-x}\text{Co}_x)\text{B} \) and \( \text{FeNi} \). \(^{17,61} \) In Fig. 8 (a) we show a cross-section of the MAE(\( \text{k} \)) (single plane going trough the \( \Gamma \)-point). The selected profile is perpendicular to the easy axis [001], crosses the high symmetry point \( \Gamma \), and is limited by the Brillouin zone boundaries. The MAE(\( \text{k} \)) cross-section is a relatively complicated map of symmetric regions consisting of positive and negative contributions. The MAE contributions observed in Fig. 8 along the orthogonal axes [100] and [010] are not equal, because the [100] direction is distinguished as quantization axis resulting in breaking of the four-fold symmetry. As the \( E_F \) is an upper integration boundary of total MAE, the FS sheets coincide with sharp changes in the \( \text{k} \)-resolved MAE contributions. It can be seen in Fig. 8 (b), where the MAE(\( \text{k} \)) 2D plot is overlapped by the corresponding section of the FS. As many of \( \text{k} \)-resolved MAE contributions is in order of \( 10^{-3} \) eV per \( \text{k} \)-point, the total MAE value of about...
FIG. 7. The band structure of Fe$_5$PB$_2$ calculated with the FPLO14 PBE+so method for quantization axes [100] (solid red lines) and [001] (dashed blue lines), together with the MAE contribution of each k-point (thick green line) as obtained by the magnetic force theorem. The high symmetry points are presented within Brillouin zone in Fig. 6 (i).

FIG. 8. (a) The cross-section of the k-resolved MAE with (b) the overlapped cross-section of the Fermi surface (black lines) for the Fe$_5$PB$_2$. The results of MAE(k) are obtained by the magnetic force theorem within the FPLO14 PBE+so method.

$10^{-4}$ eV/f.u. (83 µeV/f.u. or 0.52 MJ m$^{-3}$) indicates a fine compensation of many bigger components. Unfortunately, this extra fine compensation and the complexity of the MAE(k) makes the ways to increase the MAE of the material difficult to predict.

F. Fully Relativistic Fixed Spin Moment Calculations for Fe$_5$PB$_2$

The MAE value for Fe$_5$PB$_2$ (0.52 MJ m$^{-3}$) is calculated with the equilibrium value of the magnetic moment (8.85 µB/f.u.). In the fixed spin moment (FSM) method the value of spin magnetic moment is considered as a parameter. The fully relativistic implementation of FSM method allows to calculate the MAE as a function of spin magnetic moment. Previously, we presented the MAE results as a function of FSM and Co concentration for the (Fe$_{1-x}$Co$_x$)$_2$B alloys.

Figure 9 presents the evolution of the MAE with the total magnetic moment $m$ for the Fe$_5$PB$_2$, together with the previous results for Fe$_5$SiB$_2$. The two MAE($m$) plots are similar in shape. Going down from an equilibrium, the corresponding MAE first increases, then it reaches maximum, to decrease finally to zero at $m$ equals zero. For Fe$_5$PB$_2$ the maximum MAE($m$) is 1.94 MJ m$^{-3}$ for a fixed total magnetic moment of 6.7 µB/f.u., which means that the optimal magnetic moment has to be reduced by about 25% with respect to the equilibrium value (8.85 µB/f.u.). Thus, the question arises, how to stabilize this reduction. A simple solution would be alloying the magnetic Fe by a non-magnetic element, which of-
-十年 results in a linear decrease of magnetization. However, alloying with a new element can severely affect the band structure, which would change also the expected value of the MAE. The smallest impact on the electronic structure should have substitutions chemically most similar to Fe and for this purpose we suggest Ru and Os of the Fe group. Another strategy could be alloying of Fe \((Z_{Fe} = 26)\) with two elements at the same time, e.g. Cr \((Z_{Cr} = 24)\) and Ni \((Z_{Ni} = 28)\), keeping a constant number of the valence electrons, which should affect the band structure the least. The above considerations, however, take into account only the band structure and neglect further issues like the crystal structure and size of the atoms, for example.

G. Magnetocrystalline Anisotropy of \((\text{Fe}_{1-x} \text{Co}_x)_{3}\text{PB}_2\)

The effect of Fe/Co alloying on the MAE is not obvious in advance, whereby the first-principles calculations are of great value in predicting the results, as has been shown previously for the \((\text{Fe}_{1-x} \text{Co}_x)_2\text{B}\)\(^{17}\) and \((\text{Fe}_{1-x} \text{Co}_x)_5\text{SiB}_2\)\(^{24}\) alloys. Figure 10 presents the MAE\((x)\) dependence for the \((\text{Fe}_{1-x} \text{Co}_x)_{3}\text{PB}_2\) system as calculated with use of the supercell method. The MAE calculations based on the supercell method proved to be one of the most accurate method for evaluation the MAE.\(^{18}\) In Fig. 10 the regions of positive and negative MAE (of perpendicular and in-plane anisotropy) are separated at Co concentration \(x \approx 0.5\). The MAE is equal 0.52 MJ m\(^{-3}\) for \(\text{Fe}_5\text{PB}_2\) and -0.51 MJ m\(^{-3}\) for \(\text{Co}_5\text{PB}_2\). Whereas, the anisotropy value close to zero observed for \(x \approx 0.5\) indicates a good soft magnetic material. Figure 10 also presents the low temperature measurements of the effective anisotropy constant \(|K_{eff}|\) carried out at 3 K for several \((\text{Fe}_{1-x} \text{Co}_x)_{3}\text{PB}_2\) compositions within the boundaries of \(0.0 \leq x \leq 0.7\). The value of \(|K_{eff}|\) is the highest (0.94 MJ m\(^{-3}\)) for \(\text{Fe}_5\text{PB}_2\) and the lowest for a Co concentration \(x \approx 0.5\). \(|K_{eff}|\) measured for \(\text{Fe}_5\text{PB}_2\) is significantly larger than the \(K_1 = 0.5\) MJ m\(^{-3}\) measured at 2 K for the single crystal.\(^{26}\) The decrease of \(|K_{eff}|\) with \(x\) is in agreement with the previous measurements for \((\text{Fe}_{0.8} \text{Co}_{0.2})_5\text{PB}_2\) suggesting that 20% Co substitution reduces the anisotropy field.\(^{23}\) Previously we also showed the corresponding \(|K_{eff}|\) results for the \(\text{Fe}_5\text{Si}_1-x\text{P}_x\text{B}_2\) system.\(^{27}\) The presented values of \(|K_{eff}|\) for \(\text{Fe}_5\text{PB}_2\) were \(\sim 0.9\) MJ m\(^{-3}\) at 10 K and \(\sim 0.65\) MJ m\(^{-3}\) at 300 K.\(^{27}\) Notice that LAS is unable to determine the sign of \(|K_{eff}|\) and thus the negative values of MAE predicted for \(x \geq 0.6\) cannot be confirmed by this method. Other methods, such as magnetometry measurements in different directions for single crystals or torque magnetometry would be preferable. Here, single crystals were not available, and up to 10 wt% of impurities were present in the samples. Therefore, given the limitation in the model and the starting material the results presented from these should be seen as semi-quantitative. Taking into account the limitations of the LAS and the supercell method, the differences between theoretical and measured MAE\((x)\) results are acceptable. We conclude, that Co alloying of \(\text{Fe}_5\text{PB}_2\) is not a good strategy to increase the MAE of this system.

H. Doping \(\text{Fe}_5\text{PB}_2\) with 5d Elements

One of the methods of tailoring the MAE is doping with 5d elements.\(^{19,62}\) Previously, we have confirmed that the 5d elements can significantly affect the MAE due to a large spin-orbit coupling.\(^{19}\) From the \(\text{Fe}_5\text{Si}_1-x\text{P}_x\text{B}_2\) and \((\text{Fe}_{1-x} \text{Co}_x)_{5}\text{PB}_2\) systems, the highest MAE is found in the \(\text{Fe}_5\text{PB}_2\) phase.\(^{27}\) Thus, it is considered as the parental compound for a further MAE engineering. The MAE of \((\text{Fe}_{0.95}\text{X}_{0.05})_{5}\text{PB}_2\) compounds \((X = 5d\) elements) is calculated using the supercell method. The
results are shown in Fig. 11, with the 5d element marked on the x axis and dashed line indicating the MAE of undoped Fe5PB2. The 5d doping has sometimes beneficial and sometimes adverse effect on MAE. Significant increase of MAE is observed for W or Re doping, similar like in the case of (Fe1−xCo2)2B alloys investigated experimentally in our previous work. The MAE grows from 0.52 MJ m−3 for Fe5PB2 to about 1.1 MJ m−3 for the compositions with W or Re, with 5% Fe substitution. Previously we have shown, that the increase in MAE observed for W and Re dopants is mainly due to the strong spin-orbit coupling of the 5d atoms, however other variations in electronic structure also affect the MAE. Although in our calculations the 5d elements are initially considered as non-magnetic, the dopants undergo spin polarization in a ferromagnetic medium and contribute to the total magnetic moment of the system. The calculated spin and orbital magnetic moments on 5d impurity show clear trend along the increasing atomic number of 5d element, see Fig. 12. The spin magnetic moment of 5d impurities are antiparallel to the Fe moments in the early 5d series, while they are parallel in the late 5d series. Corresponding trends for 5d atoms in magnetic 3d hosts have been found previously computationally and experimentally.

IV. SUMMARY AND CONCLUSIONS

Our considerations began with a detailed theoretical analysis of the Fe5PB2 compound. The Fe 3d orbitals are dominant in the valence band and responsible for the formation of large magnetic moments. For the Fe5PB2 the fully relativistic band structure in the vicinity of Fermi level was considered to better understand the origin of the high value of magnetocrystalline anisotropy energy (MAE). The calculated Fermi surface requires experimental confirmation. The results of fully relativistic fixed spin moment calculations suggested that reduction of the magnetic moment of Fe5PB2 should induce about fourfold increase of the MAE. For practical realization of magnetic moment reduction it is suggested to alloy Fe with a non-magnetic element Ru or Os from the Fe group, or to partially replace Fe with two elements at once, Cr and Ni, for example, keeping constant number of valence electrons.

Three critical parameters for technological applications: saturation magnetization (\(M_S\)), Curie temperature (\(T_C\)), and MAE were calculated for the whole concentration range between Fe5PB2 and Co5PB2. The calculated \(M_S\) and \(T_C\) decreased with Co concentration and for the terminal composition Co5PB2 a weakly ordered magnetic ground state was predicted. The calculated \(M(x)\) and \(T_C(x)\) were in decent agreement with the measurements, although the ferromagnetic ground state of Co5PB2 is questionable. The Co doping in (Fe1−xCo2)5PB2 system gives the possibility of tuning the \(T_C\) in a range from about six hundred kelvins to almost down to zero. The calculated MAE was positive for Fe5PB2, negative for Co5PB2, and went through zero around 50% Co concentration. This picture of MAE(x) behavior was in overall agreement with the experimental study of the effective anisotropy constant |\(K_{eff}\)| for the (Fe1−xCo2)5PB2 alloys. The measurements showed the highest |\(K_{eff}\)| value for stoichiometric Fe5PB2 which decreased with Co doping. We concluded then that Co alloying is not a good strategy to increase the MAE of Fe5PB2 alloy. The measured |\(K_{eff}\)| of about 0.94 MJ m−3 at 3 K was, however, the highest value obtained so far for Fe5PB2, giving a hope for potential application of its other alloys. It was also calculated how the 5% doping of Fe with 5d elements affects the MAE of the Fe5PB2. It was shown that Fe5PB2 doping with W or Re results in significant increase of the MAE.

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