Intrinsic Magnetic Properties of a Highly Anisotropic Rare-Earth-Free Fe$_2$P-Based Magnet

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Permanent magnets are applied in many large-scale and emerging applications and are crucial components in numerous established and newly evolving technologies. Rare-earth magnets exhibit excellent hard magnetic properties; however, their applications are limited by the price and supply risk of the strategic rare-earth elements. Therefore, there is an increasing demand for inexpensive magnets without strategic elements. Here, the authors report the intrinsic highly-anisotropic magnetic properties of Co and Si co-doped single crystals (Fe$_{1-x-y}$Co$_x$)$_2$P$_{1-z}$Si$_z$ (y = 0.09). Co increases Curie temperature $T_C$; Si doping decreases magnetocrystalline anisotropy $K_1$ and also increases $T_C$ significantly because of the enhanced interlayer interaction. The maximum room temperature magnetocrystalline anisotropy $K_1 = 1.09$ MJ m$^{-3}$ is achieved for $x = 0.22$, with saturation magnetization $\mu_0M_s = 0.96$ T and $T_C = 506$ K. The theoretical maximum energy product is one of the largest for any magnet without a rare earth or Pt. Besides its promising intrinsic magnetic properties and absence of any strategic elements, other advantages are phase stability at high temperatures and excellent corrosion resistance, which make this material most promising for permanent magnetic development that will have a positive influence in industry and daily life.

1. Introduction

Permanent magnets are now established as crucial components of modern electromagnetic technology with many existing large-scale and emerging applications, such as hard disks, wind turbines, robotics, and electric vehicles. Typically, permanent magnetic materials are ferromagnetic or ferrimagnetic materials, which are characterized by a large hysteresis, as shown schematically in Figure 1a. Among the intrinsic material properties, the most important are: i) the Curie temperature ($T_C$), above which the cooperative magnetism disappears; ii) the saturation magnetization ($\mu_0M_s$), which is decisive for the remanence $B_r$ and the energy product $(BH)_{\text{MAX}}$; and iii) the uniaxial magnetocrystalline anisotropy $K_1$, which determines the magnetic hardness parameter $\kappa = \sqrt{K_1/(\mu_0M_s)}$, a convenient figure of merit for permanent magnets related to coercivity $H_C$. For a good permanent magnet with useful coercivity, $\kappa$ should be larger than $1$.\footnote{1}

High performance rare-earth permanent magnets such as Sm-Co and Nd$_2$Fe$_{14}$B offer good values of all three intrinsic properties and are widely used in our daily lives and for industrial applications. Despite their excellent properties, applications are limited by the high price and the supply risk of the strategic rare-earth elements as shown in Figure 1b. Commercial rare-earth-free alternatives are ferrites (BaFe$_{12}$O$_{19}$ or SrFe$_{12}$O$_{19}$), which are produced on a large scale, and Alnico magnets.\footnote{2} However, their maximum energy product $(BH)_{\text{MAX}}$ is only one-tenth that of the rare-earth magnets owing to either low $\mu_0M_s$ or small $K_1$. Therefore, it is important to find inexpensive magnets to fill the gap between rare-earth magnets and ferrites/Alnico.\footnote{3}

Tetragonal Li$_0$, CoPt or FePt\footnote{4} can exhibit both large $\mu_0M_s$ and $K_1$. However, the high platinum content is economically prohibitive for most purposes. Other candidates for rare-earth-free magnets include Mn-based compounds MnAl,\footnote{5} Mn$_2$Ga,\footnote{6} and MnBi\footnote{7} and Co-based compounds Zr$_2$Co$_{11}$ and HfCo$_7$.\footnote{8} Mn-based compounds contain no critical elements and are thus relatively inexpensive. Unfortunately, all these materials have thermal-stability problems, which make it difficult to synthesize a pure phase on a large scale, and almost impossible to make sintered magnets with high density, thereby limiting their
possible application. In addition, the problem of twinning in CoPt, FePt, MnAl, and Mn$_2$Ga makes it difficult to align the powders to optimize their theoretical performance.

Since Fe is the most abundant 3d element and has the lowest price, it is desirable to find Fe-based rare-earth-free magnets. Pure iron is a body-centered-cubic and its high-symmetry crystal structure excludes uniaxial anisotropy. Hence, alloys or compounds with a uniaxial crystal structure, such as hexagonal or tetragonal, are needed as shown in Figure 1c. The key to designing a rare-earth-free magnet is to find the right partner for iron. Generally, light elements are abundant on earth, and usually cheap, particularly those in the first three periods, many of which are rock-forming elements. Intermetallic compounds consisting of iron and alkali (Li and Na) or alkaline-earth metal...
Among the iron pnictides, Fe$_2$P simultaneously exhibits a large $K_1$ (2.32–2.68 MJ m$^{-3}$) and a $\mu_B M_s$ of 1.03 T\cite{11,12} which is promising. It crystalizes in the non-centrosymmetric hexagonal space group P6$_2$2m (189). The crystal structure combines two alternating layers with two inequivalent Fe and P sites as shown in Figure 2. Each Fe1 atom (in the tetrahedral sites) only has two Fe1 as its nearest neighbors and hence, the interaction between Fe1–Fe1 is negligible; meanwhile, each Fe2 atom (in the pyramidal site) has four Fe2 as its nearest neighbors and six Fe1 atoms at almost the same distance. Therefore, the dominant exchange is a strong ferromagnetic Fe2–Fe2 interaction and a weaker but still strong Fe1–Fe2 interaction.\cite{13} This results in a large localized magnetic moment of $\approx 2 \mu_B$ for Fe2 and a small itinerant moment of less than $\mu_B$ for Fe1.\cite{12,14}

The Curie temperature ($T_C$) of Fe$_2$P is only 214 K. Therefore, significant efforts have been made to raise its $T_C$ above room temperature. Enhancing the weak ferromagnetism of Fe1 is key and can be realized using two possible methods. The first method enhances the weak ferromagnetism of Fe1 by doping with Co because of the stronger exchange of Co compared with Fe. It was reported that 15% of the iron in Fe$_2$P can be replaced by cobalt while maintaining the hexagonal structure\cite{15} (more Co leads to an orthorhombic structure). Cobalt-doped Fe$_2$P has a Curie temperature of up to 441 K, a $B_r$ of $\approx 0.4$ T, and a $K_1$ of 0.31 MJ m$^{-3}$ at room temperature.\cite{16} However, this Co-doped Fe$_2$P is of little interest for hard magnet applications because these values are smaller than those of ferrite. The second method enhances the interaction between Fe1 and Fe2 by decreasing the distance between each layer through doping at the P site. Substituting P with S$_x$\cite{17,18,19,20} As$_{x}$\cite{19,20}, Ge$_{x}$\cite{21} and B\cite{18,19,22} (Fe$_{1-x}$P$_{1-x}$Z$_x$, $Z$ = Si, As, Ge, and B) in Fe$_2$P has been found to increase $T_C$, but at the cost of a decrease in $K_1$ and the appearance of competing orthorhombic and cubic structures. These phases are not magnetically hard, and accordingly, their formation and presence alongside the hexagonal Fe$_2$P phase is undesirable. Co-doping of Fe$_2$P with Co (or Ni) and Si has also been studied using calculations\cite{13} to predict the peak of the anisotropy exhibited in the composition containing 7–10% Co (or 3.5–5% Ni) and 14–20% Si. Guillou et al. reported on mixtures with Si, Co, and Ni doping in polycrystalline materials using ball milling.\cite{22,23} These mixtures do not represent a homogeneous compound with a unique crystal structure. Rather the mixture includes secondary phases, as evidenced by x-ray diffraction (XRD) and the magnetization versus temperature curves. Up to now, neither the exact composition, nor the intrinsic magnetic property of these mixtures has been clarified.

Here, we report the intrinsic magnetic properties of single crystals of (Fe$_{1-x}$Co$_x$)$_2$P$_{1-x}$Si$_x$ ($y \approx 0.09$). The $T_C$ increases monotonically with increasing $x$. Both a large $K_1$ of 1.09 MJ m$^{-3}$ and a $\mu_0 M_s$ of 0.96 T are simultaneously achieved at room temperature for $x = 0.22$, where $T_C$ is as high as 506 K. The

\( \text{(Mg) do not exist. Fe-based compounds with halogens (F and Cl) and chalcogens (O and S) are mainly antiferromagnetic or ferrimagnetic with boron group (B and Al), carbon group (C and Si), and pnictogens (N and P) are ferromagnetic, and some candidates for hard magnets as shown in Figure 1d.}\)

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theoretical \( (BH)_{\text{MAX}} \) is 204 kJ m\(^{-3} \) for \( x = 0.26 \), one of the largest values in highly anisotropic materials without rare earth or Pt. These are promising for permanent magnets.

2. Results and Discussion

Single crystals (shown in Figure S1, Supporting information, and Table 1) of Co and Si co-doped Fe\(_2\)P were grown using the Sn-flux method.\(^{[25]} \) Co-doping Co and Si stabilizes the hexagonal structure and the solution limit for Si is extended to \( \approx 26\% \) for the P site in the equilibrium state for \((\text{Fe}_{1-y}\text{Co}_y)_{2}\text{P}_{1-x}\text{Si}_x\) \((y \approx 0.09)\), compared with only 20\% in \( \text{Fe}_2\text{P}_{1-x}\text{Si}_x\) .\(^{[17]} \) The lattice constant \( c \) shrinks by 1.6\% when \( x \) increases from 0.08 to 0.26, which could enhance the interlayer interaction.

Figure 3 shows the magnetization curves along the \( c \) and \( a \) axes at 2 and 300 K. The \( c \) axis magnetization saturates immediately after the field is applied, whereas a large magnetic field is required to saturate the magnetization along the \( a \) axis, thus revealing a typical uniaxial anisotropy. These crystals show anisotropic saturation magnetization owing to the large \( K_1 \), where the magnetization along the \( c \) axis \( M_{sc} \) is \( \approx 6\% - 12\% \) larger than that along the \( a \) axis \( (M_{sa}) \), similar to the 9\% in binary \( \text{Fe}_2\text{P} \).\(^{[12]} \) Increasing \( x \) from 0.11 to 0.26 at 2 K slightly increases the \( c \) axis polarization from 1.09 to 1.15 T, whereas at 300 K it increases more obviously from 0.84 to 1.01 T. The polarization obtained at low

Table 1. Composition and lattice constants.

| Final product       | Method              | Starting materials | Fe  | Co  | P     | Si  | Sn | Lattice constant |
|---------------------|---------------------|--------------------|-----|-----|-------|-----|----|-----------------|
|                     |                     |                    |     |     |       |     |     | \( a (\text{Å}) \) | \( c (\text{Å}) \) | \( c/a \) | \( V [\text{Å}^3/\text{f.u.}] \) |
| \((\text{Fe}_{0.88}\text{Co}_{0.12})_{2}(\text{P}_{0.92}\text{Si}_{0.08})\) | Melting and etching |                   | 1.78| 0.22| 0.89  | 0.11| –  | 5.881(6)       | 3.433(5) | 0.583 | 34.287          |
| \((\text{Fe}_{0.91}\text{Co}_{0.09})_{2}(\text{P}_{0.89}\text{Si}_{0.11})\) | Flux                |                   | 1.80| 0.20| 0.80  | 0.30| 20 | 5.895(1)       | 3.417(5) | 0.583 | 34.484          |
| \((\text{Fe}_{0.91}\text{Co}_{0.09})_{2}(\text{P}_{0.86}\text{Si}_{0.14})\) | Flux                |                   | 1.80| 0.20| 0.78  | 0.22| 20 | 5.923(3)       | 3.415(3) | 0.576 | 34.590          |
| \((\text{Fe}_{0.91}\text{Co}_{0.09})_{2}(\text{P}_{0.81}\text{Si}_{0.19})\) | Flux                |                   | 1.80| 0.20| 0.73  | 0.27| 20 | 5.934(1)       | 3.407(8) | 0.574 | 34.640          |
| \((\text{Fe}_{0.91}\text{Co}_{0.09})_{2}(\text{P}_{0.78}\text{Si}_{0.22})\) | Flux                |                   | 1.80| 0.20| 0.67  | 0.33| 20 | 5.954(2)       | 3.396(5) | 0.570 | 34.760          |
| \((\text{Fe}_{0.91}\text{Co}_{0.09})_{2}(\text{P}_{0.74}\text{Si}_{0.26})\) | Flux                |                   | 1.80| 0.20| 0.61  | 0.39| 20 | 5.969(0)       | 3.379(3) | 0.566 | 34.755          |
| –                   | Flux                |                   | 1.78| 0.22| 0.56  | 0.44| 20 | No single crystal |           |      |                 |
| –                   | Flux                |                   | 1.80| 0.20| 0.50  | 0.50| 20 | \( \text{Fe}_2\text{P} + \text{Fe}_2\text{Si} + \text{Fe}_5\text{Si}_3 \) |

Figure 3. Magnetization curves along the \( c \) and \( a \) axes at 2 and 300 K for a) \( x = 0.11 \), b) 0.19, c) 0.22, and d) 0.26. The small-field hysteresis loop can be found in the domain pattern in Figure S2, Supporting information. The magnetization along the \( c \) axis \( M_{sc} \) is always a few percent larger than that along the \( a \) axis \( (M_{sa}) \).
temperatures is significantly larger than that in binary Fe$_2$P of 1.03 T.$^{[11,12]}$ The anisotropy field $B_a$ monotonically decreases from 6.2 to 3.4 T with increasing $x$ from 0.11 to 0.26 at 2 K, whereas at 300 K it increases from 2.3 to 2.8 T from $x = 0.08$ to 0.22 and then falls back to 2.3 T for $x = 0.26$. The corresponding $K_1 = \frac{1}{2}M_sB_a$ decreases from 2.68 ($x = 0.08$) to 1.56 MJ m$^{-3}$ ($x = 0.26$) at 2 K, and increases from 0.77 ($x = 0.08$) to 1.09 MJ m$^{-3}$ ($x = 0.22$) followed by a decrease to 0.93 MJ m$^{-3}$ ($x = 0.26$) at 300 K. For all compositions, the room temperature $\kappa$ is always larger than 1, which is the practical threshold for considering for permanent magnet development.

The magnetic structure of the doped Fe$_2$P single crystals are shown in Figure S2. Supporting information. The needle-like single crystals for $x = 0.11$ (5 mm long and 0.2 mm wide) on the (100) surface are a single-domain in the remanent state, which confirms uniaxial anisotropy. During demagnetization, there are several Barkhausen jumps due to the nucleation and stepwise growth of the inverse domains. To verify that $K_1$ is large enough to resist self-demagnetization in any shape, the domain structure of the (0001) plane on a thin lamella of 70 nm thick ($N = 1$) was observed in a Lorentz transmission electron microscope. Maze domains (sometimes called stripe or band domains) were observed at zero field, which became bubbles at 0.3 T applied along $c$. This behavior is similar to that of many hard magnetic materials such as L1$_0$ Fe-Pt,$^{[26]}$ ferrite,$^{[27]}$ and MnBi.$^{[28]}$

The temperature-dependent magnetization curves for two compositions are shown in Figure S3, Supporting information. Despite the increased $T_C$ with $x$, hysteresis between heating and cooling was observed at $T_C$, indicating that the magnetic transition is a first-order transition like binary Fe$_2$P.$^{[15]}$ The hysteresis is more obvious in a low Si concentration sample, indicating that Si doping suppressed the first-order magnetoelectric coupling. A detailed characterization of the critical phenomena around $T_C$ was performed for (Fe$_{0.92}$Co$_{0.08}$)$_2$(P$_{0.78}$Si$_{0.22}$) using the initial isothermal $M(H)$ curves, as shown in Figure S4, Supporting information. The critical exponents of $\beta = 0.25$, $\gamma = 1.0$, and $\delta = 5.0$ were obtained, which matches with the tricritical model$^{[29]}$ indicating that the ferromagnetic phase transition for a high Si content is at the boundary between the first-order and the second-order phase transitions.$^{[30]}$ This is different with Mn and Si co-doped Fe$_2$P$^{[12,25]}$ which is studied for magnetocaloric effects with a thermal hysteresis of more than 50 K. Si doping also suppresses the short-range-ordered magnetic structure above $T_C$ from the inverse susceptibilities $\chi^{-1}$ shown in Figure S3e,f, Supporting information.

The local structure and magnetic properties of (Fe$_{1-y}$Co)$_2$P$_{1-x}$Si$_x$ ($y = 0.09$) were studied by $^{57}$Fe Mössbauer spectroscopy at room temperature and 6 K, as shown in Figure S5, Supporting information. The composition-dependent hyperfine field is more obvious in Fe2. With increasing $x$ from 0.11 to 0.26, the hyperfine field at Fe2 increases from 15.6 to 16.9 T at room temperature, and from 18.6 to 19.3 T at 6 K, respectively. Note that these values are larger than those in (Fe$_{0.8}$Co$_{0.2}$)$_2$P (13.2 T)$^{[31]}$ and in Fe$_{2}$P$_{0.8}$Si$_{0.2}$ (14.7 T)$^{[32]}$ at room temperature, illustrating that Co and Si co-doping significantly increase the moment, agreeing with the magnetization curves in Figure 3.

The intrinsic magnetic properties with different $x$ values are summarized in Figure 4 and Table 2. Si doping slightly enhances the $\mu_0M_s$ at 2 K, but $K_1$ obviously decreases, whereas $T_C$ greatly increases. Therefore $\mu_0M_s$ increases monotonically at room temperature with increasing $x$ (mainly due to $T_C$). The maximum room temperature $K_1$ is achieved when $x = 0.22$ owing to a combination of a decrease in the intrinsic $K_1$ and an increase in $T_C$ with increasing $x$, resulting in $\mu_0M_s$, $K_1$, and $T_C$ of 0.96 T, 1.09 MJ m$^{-3}$, and 506 K, respectively, confirming a previous prediction.$^{[13]}$

Our first principles calculations (Figure S6, Supporting information) reveal that the interaction between Fe2–Fe2 decreases slightly with increasing $x$ owing to the large in-plane distance related to a large $a$. However, the interlayer interaction between Fe1 and Fe2 drastically increases because of the decrease in $c$, which is the main reason for the increased $T_C$. Meanwhile, the anisotropy quickly decreases owing to the shortened interlayer distance, agreeing with previous calculations.$^{[31]}$ Unfortunately, the demands for enhanced $K_1$ and $T_C$ have an opposite effect on the lattice constants; therefore, a compromise is necessary and the best room-temperature properties are exhibited with $x = 0.22$.

The theoretical $(BH)_{MAX}$ at room temperature, which is calculated as $\frac{1}{2}\mu_0M_s^2$, for hard magnetic materials with $\kappa > 1$ at room temperature is shown in Figure 5. The largest value we have found in our system is $(BH)_{MAX} = 204$ kJ m$^{-3}$ with the $x = 0.26$, which has a lower $K_1$ than $x = 0.22$, but a higher magnetization. Co and Si co-doped Fe$_2$P fills the gap between the expensive rare-earth magnets and cheap but poor-performance ferrite magnets.$^{[33]}$ Among all the gap magnets, Fe$_2$P exhibits the largest theoretical $(BH)_{MAX}$, which is almost double those of MnBi and MnAl and four times that of ferrite.

We have made an isotropic bonded magnet by ball milling. Though its coercivity is small ($\mu_0H_c = 0.05$ T) due to the large grain size (2–5 μm), it can easily lift up an iron rod (Supporting Information video). The single domain limit size can be estimated by $36\kappa\sqrt[3]{[\mu_0M_s]}/[A]$, where the exchange constant $A$ of 5 J m$^{-3}$ is deduced from $T_C$. It is $110–130$ nm in doped Fe$_2$P, which is similar to the 110 nm in Nd$_3$Fe$_4$B. Future work is required to control the grain size and to find a suitable phase at the grain boundary to achieve the large coercivity and square hysteresis loop required for a real magnet.

Unlike intermetallic magnets like Nd$_3$Fe$_4$B or oxide-based magnets like Ba ferrite, Fe$_2$P is extremely stable in a corrosive (strong acidity and oxidative) environment. The doped compounds do not react with concentrated HCl (18%), HNO$_3$ (67%), or H$_2$SO$_4$ (98%) as shown in Figure S7, Supporting information. This chemical stability allows the material to be used in extreme conditions without additional coating for protection.

The thermal stability of doped Fe$_2$P was also verified by melting the single crystals with $x = 0.11$, as shown in Figure S7, Supporting information. There is no structural transition below the melting point of 1520 K, which is promising for sintered magnets with a high density.

3. Conclusion

In conclusion, we report the intrinsic highly anisotropic magnetic properties of (Fe$_{1-y}$Co)$_y$P$_{1-x}$Si$_x$ ($y = 0.09$) single crystals. Co-doping Co and Si stabilizes the hexagonal structure. Though Si doping decreases the $K_1$ at 2 K, the $T_C$ greatly increases
owing to the enhanced interlayer exchange interaction. The maximum room temperature $K_1$ is achieved when $x = 0.22$ owing to a combination of these two effects. Si also suppresses the first-order character of the transition at the $T_c$ and a short-range order above the $T_c$. Co and Si co-doped Fe$_2$P is promising for hard magnetic applications, filling the gap between rare-earth magnet and ferrite. The advantages of Fe$_2$P for permanent magnets are:

1. Highly anisotropic magnetic performance at room temperature. The best composition is $x = 0.22$, which exhibits a large $\mu_0 M_s$ and $K_1$ of 0.96 T and 1.09 MJ m$^{-3}$, respectively, at room temperature and a $T_c$ of 506 K. Though with a slightly smaller $K_1$, $x = 0.26$ sample shows the highest $T_c = 560$ K and the largest $\mu_0 M_s = 1.01$ T and its theoretical $(BH)_{\text{MAX}}$ is the largest among all gap magnets, and is twice that of MnBi and MnAl and four times that of ferrite.

**Table 2.** Intrinsic magnetic properties at 2 and 300 K. $\theta_p$ means paramagnetic Curie temperature.

| Composition | $\mu_0 M_s$ [T] (2 K) | $\mu_0 M_s$ [T] (300 K) | $K_1$ [M m$^{-3}$] (2 K) | $B_s$ [T] (2 K) | $K_1$ [M m$^{-3}$] (300 K) | $B_s$ [T] (300 K) | $T_c$ [K] | $\kappa$ (300 K) | $(BH)_{\text{MAX}}$ [kJ m$^{-3}$] in theory | $\theta_p$ [K] (c axis) |
|-------------|----------------------|------------------------|------------------------|----------------|------------------------|----------------|----------|---------------|---------------------------------|----------------|
| (Fe$_{0.91}$Co$_{0.09}$)$_2$(P$_{0.89}$Si$_{0.11}$) | 1.09 | 0.84 | 2.68 | 6.2 | 0.77 | 2.3 | 414 | 1.16 | 141 | 479 |
| (Fe$_{0.91}$Co$_{0.09}$)$_2$(P$_{0.86}$Si$_{0.14}$) | 1.11 | 0.90 | 2.17 | 4.9 | 0.86 | 2.4 | 454 | 1.15 | 162 | 462 |
| (Fe$_{0.91}$Co$_{0.09}$)$_2$(P$_{0.81}$Si$_{0.19}$) | 1.09 | 0.92 | 1.97 | 4.5 | 0.89 | 2.4 | 474 | 1.14 | 170 | 485 |
| (Fe$_{0.92}$Co$_{0.08}$)$_2$(P$_{0.78}$Si$_{0.22}$) | 1.10 | 0.96 | 2.00 | 4.5 | 1.09 | 2.8 | 506 | 1.20 | 183 | 522 |
| (Fe$_{0.91}$Co$_{0.09}$)$_2$(P$_{0.74}$Si$_{0.26}$) | 1.15 | 1.01 | 1.56 | 3.4 | 0.93 | 2.3 | 560 | 1.07 | 204 | 562 |
| Fe$_2$P | 1.03 | – | 2.68 | 6.5 | – | – | 214 | – | – | 395 |

**Figure 4.** Magnetic properties. a) Temperature-dependent saturation magnetization along the $c$ axis obtained under an applied magnetic field of 1 T. b) Temperature-dependent $K_1$. c) $T_c$ and the average hyperfine fields monotonically increase with $x$ at 300 K. d) $\mu_0 M_s$ monotonically increases with $x$ at 300 K, whereas the maximum $K_1$ occurs at $x = 0.22$. 
3. Thermal stability. No structural phase transition occurs and prevent the growth of single crystals. As a result, polycrystalline product was 26%. Additional Si in the starting material led to secondary Si-rich phases, like Fe₃Si and Fe₅Si₃, which segregate the Fe₂P seeds and the remaining flux on the surface was removed using HCl. The crystal structure and composition were confirmed using XRD, wavelength dispersive X-ray spectroscopy (WDX), and energy-dispersive X-ray spectroscopy (EDX). In the differential scanning calorimeter (DSC) measurement, 5 mg of single crystals were heated up to 1773 K in vacuum at 10 K min⁻¹.

Polycrystalline Preparation: Polycrystalline Fe₀.₈₈Co₀.₁₂(P₀.₉₂S𝑖₀.₀₈) was prepared using the melting and etching method. The starting materials were Fe₂P powders (99.5%), Co, and Si. They were mixed in a BN crucible (the melting liquid react with alumina), which was sealed in an evacuated Ta tube. The Ta tube was heated in Ar atmosphere to 1773 K in 24 h, held for 24 h, and then cooled down in an oven. The obtained ingot was ground into powder and then transferred into HCl (e.g., 18 wt%) for 24 h to remove the Fe-rich secondary phase, which was typically present in the initial ingot in an amount of ≈2–4 vol%.

Mössbauer Spectroscopy: ⁵⁷Fe Mössbauer spectra were collected at 6 and 293 K with a standard WissEl spectrometer, which was operated in the constant acceleration mode with a ⁵⁷Co/Rh source. About 20 mg of sample were mixed with boron nitride in a plexiglass sample container with a diameter of 13 mm. The sample holder was placed in a JANIS SHI-850-5 closed cycle refrigerator. The spectra were evaluated with the program MossWinn. Isomer shifts were referred to alpha-iron.

Magnetic Domain Observation: Magnetic domain images were obtained for a bulk single crystal using the polar Kerr effect in a wide-field magneto-optical Kerr microscope at room temperature on a (11100) surface. The domain images for a thin lamella on a (0001) surface were obtained using Lorentz transmission electron microscopy. The magnetic phases were imaged using a double-corrected FEI Titan™ 80–300 and a JEOL Jem F-200C transmission electron microscope operated in the Lorentz mode at acceleration voltages of 300 and 200 kV, respectively.

First-Principles Calculations: The electronic and magnetic structures were calculated using the first principles computer program SPRKKR in the local spin density approximation. The full potential, fully relativistic mode of the program was used.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.
Author Contributions
The single crystals were grown by Y.H. and Q. M. The crystal and magnetic properties were characterized by Y.H. with the help of H.B. and W.S. G.H.F. provided theoretical support. The magnetic domain structures were characterized by S.S., I. S., R.S., and B.R. The Mössbauer spectra were measured and analyzed by P.A. The manuscript was written by Y.H. and G.H.F., with feedback from all the authors. The project was supervised by C.F.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author on reasonable request.

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Fe2P, magnetocrystalline anisotropy, permanent magnets, single crystals

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