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MAGNETIC PROPERTIES OF $(Fe,Co)_5SiB_2$ ALLOYS BY W DOPING

R. HIRIAN[1*], V. POP[2], O. ISNARD[2,3], D. BENEA[1]

ABSTRACT. The intrinsic magnetic properties (magnetic moments, magneto-crystalline anisotropy, Curie temperatures) of the $Fe_{5-x-y}Co_yW_xSiB_2$ alloys have been calculated using the spin-polarized relativistic Korringa-Kohn-Rostoker (SPRKKR) band structure method. Our calculations show that for several compounds with $x \geq 0.5$, the magnetocrystalline anisotropy energy (MAE) became axial. Also, theoretical calculations for Fe_4WSiB_2 compound found a magnetization decrease (with about 20%), a Curie temperature decrease of about 30% but an increased axial magnetocrystalline anisotropy compared with the corresponding values for Fe_5SiB_2. Several $Fe_{5-x}W_xSiB_2$ alloys (x = 0, 0.1, 0.2, 0.5, 1) have been prepared by arc melting of corresponding high purity elements in Ar controlled atmosphere. Composition analysis of the $Fe_{5-x}W_xSiB_2$ alloys found an impurity phase along with the tetragonal *I4/mcm* phase of pure Fe_5SiB_2. The magnetic measurements found the decrease of the magnetization any significant increase of the coercivity due to W doping.

Keywords: *ab-initio calculations, B. magneto-crystalline anisotropy, C. magnetization, D. rare earth free magnets.*

INTRODUCTION

Magnetic materials are main components of many devices, and their development, impact and innovation are crucial on raising energy efficiency in many economic sectors. Permanent magnets are used widely in advanced technologies

[1] *Faculty of Physics, Babeş-Bolyai University, Cluj-Napoca, Kogălniceanu str. 1, 400084 Cluj-Napoca, Romania.*
[2] *Université Grenoble Alpes, Institut Néel, Grenoble, F-38042, France.*
[3] *CNRS, Institut Néel, 25 rue des Martyrs, F-38042 Grenoble, France.*
* *Corresponding author: razvan.hirian@ubbcluj.ro*

including electric vehicles, memory devices, electric motors, windmills, transportation, magnetic levitation or biomedical devices (including magnetic resonance imaging machines, pacemakers, heart pumps, etc.). A route to build performant magnets with lower prices is to develop rare-earth-free magnets that can fill in the gap between the chip hard ferrite and high performant by expensive rare-earth magnets [1].

A promising class of materials which can be explored is based on Fe_5SiB_2 alloy, due to their intrinsic properties (Tc > 800 K, M_s ~ 9 μ_B/f.u. and K_1~-0.30 MJ/m^3). According to our previous studies [2], the magnetization decreases at 1.46 μ_B/f.u. in Co_5SiB_2 alloys. Also, the Curie temperature is reduced by Co for Fe substitution [2]. The magnetocrystalline anisotropy energy (MAE) is negative for Fe_5SiB_2, but its absolute magnitude decreases by Co for Fe substitution. To build performant permanent magnets, the materials should have (i) ferromagnetic ordering with a high Curie temperature, (ii) large saturation magnetization and (iii) a strong magnetic anisotropy of the easy-axis type [3], first two conditions being fulfilled by Fe_5SiB_2 alloy. The Co for Fe substitution in $Fe_{5-x-y}Co_yW_xSiB_2$ is able to turn the sign of MAE from negative to positive for $1.5 \leq y \leq 2.5$, enabling an axial easy magnetization axis for the corresponding alloys [2]. On the other hand, previous studies [4] showed that doping of Fe_5PSi_2 alloy with a *5d* element would induce a strong uniaxial anisotropy, allowing to build a semi-hard magnet which can be used in nanocomposite magnetic materials. In the present study the W doping of the $Fe_{5-y}Co_ySiB_2$ alloys has been considered, accounting for both axial anisotropy of the alloys with $1.5 \leq y \leq 2.5$ as well as for the strong spin-orbit coupling of the *5d* element which could enhance the axial anisotropy of the W doped alloys. Theoretical and experimental studies on the structural and magnetic properties of $Fe_{5-x-y}Co_yW_xSiB_2$ alloys are presented in the following.

COMPUTATIONAL AND EXPERIMENTAL DETAILS

Spin-polarized fully relativistic Korringa-Kohn-Rostoker (SPRKKR) band structure method has been used for theoretical calculations [5]. The exchange and correlation effects have been accounted for by means of the generalized gradient approximation with the parametrization of Perdew et al. (GGA-PBE) [6]. The k-space integration was performed using the special points method [7]. The substitutional disorder in the system has been treated within the Coherent Potential Approximation (CPA) theory [8]. The study of the magnetic anisotropy has been performed by magnetic torque calculations acting on the magnetic moment $\overrightarrow{m_i}$ of the atomic site *i,* oriented along the magnetization direction $\vec{M}$ [9,10]. The component of the magnetic

torque with respect to axis $\hat{u}$ is $T_{\hat{u}}(\theta,\varphi) = -\partial E(\overrightarrow{M}(\theta,\varphi))/\partial\theta$, where θ and φ are the polar angles. The magnetic torque and the energy difference between the in-plane and out-of-plane magnetization directions are related by a special geometry. By setting the angles to $\theta = \pi/4$ and $\varphi = 0$, the calculated magnetic torque is $T_{\hat{u}}(\pi/4,0) = E_{[100]} - E_{[001]}$ [10]. A complementary approach to investigate the magnetic behaviour of is based on the classical Heisenberg Hamiltonian described by the expression:

$$H_{ex} = -\sum_{ij} J_{ij}\hat{e}_i \cdot \hat{e}_j ,$$

where the summation is performed on all lattice sites *i* and *j* and $\hat{e}_i$ / $\hat{e}_j$ are the unit vectors of magnetic moments on sites *i* and *j,* respectively. The J_{ij} exchange coupling parameters for all magnetic atoms have been calculated as a function of distance using the expression derived by Liechtenstein [11] based on the magnetic force theorem. The Curie temperatures have been derived using the J_{ij} exchange coupling parameters within the mean field approach [11,12],

$$T_c^{rough-MFA} = \frac{2}{3k_B}\sum_i J_{0i} ,$$

where J_{0i} is the exchange-coupling parameters sum over all coordination shells up to 15 Å around lattice site *i*.

The synthesis of the polycrystalline $Fe_{5-x}W_xSiB_2$ alloys (x = 0, 0.1, 0.2, 0.5, 1) alloys has been performed following the arc melting procedure described elsewhere [2] starting from high purity elements (99.999% Fe, 99.99% Si, 99.5% W, 99.7% B), under high purity Ar atmosphere. Each sample was turned and re-melted several times, to ensure homogeneity.

The crystalline structure of the samples was investigated by X-Ray diffraction (XRD), using a Bruker D8 Advance diffractometer equipped with a Cu K_α radiation. The phase content of the annealed alloys was determined using the Rietveld method. In order to compare the data recorded with different wavelengths, the XRDs are plotted versus $1/d_{hkl}$. The lattice parameters of the different samples were determined using the Celref 3 software [13] from least square measurements taking all the Bragg peaks observed into account. Magnetization measurements were carried out using a VSM magnetometer in applied field of up to 4 T (4 K – 300 K).

RESULTS AND DISCUSSIONS

The electronic band structure calculations for the $Fe_{5-x-y}Co_yW_xSiB_2$ (x = 0.0, 0.15, 0.25, 0.5, 1.0; y = 0.0, 1.0, 1.5 and 2.0;) in tetragonal structure (space group *I4/mcm*) using the experimental lattice parameters [2, 14] have been performed. The lattice constants of the W-doped alloys have been evaluated using the experimental lattice constants [2,14,15] and considering their linear dependence with W content x. The random occupation of W atoms of the *4c* and *16l* crystal sites has been considered. Calculated magnetic moments (in Bohr magnetons μ_B) for the $Fe_{5-x-y}Co_yW_xSiB_2$ (x = 0, 0.15, 0.25, 0.5, 1.0 and y = 0, 1.0, 1.5 and 2.0) are shown in Table 1.

According to our calculations, Fe_5SiB_2 alloy is ferromagnetic with a total magnetic moment of 9.24 μ_B/f.u., in plane easy axis with the calculated anisotropy constant K_1 = -0.206 meV/f.u.. The Curie temperature calculated by mean field approach is 1140 K. As the mean field method is known to overestimate by ~20% the Curie temperature values, the estimated T_c would be comparable with the experimental value of 850 K [2].

Table 1. Calculated magnetic moments, MAE constant K_1 and the estimated Curie temperature for the $Fe_{5-x-y}Co_yW_xSiB_2$ alloys (x = 0.0, 0.15, 0.25, 0.5, 1.0; y = 0.0, 1.0, 1.5 and 2.0). Preferential occupation of W for *4c* sites has been considered

	lattice const. *a,c* (Å)	**m_s (μ_B/f.u.)**	**m_l (μ_B/f.u.)**	**K_1 (meV/f.u.)**	**T_c (K)**
Fe_5SiB_2	5.5446; 10.336	9.03	0.215	-0.206	1140
$Fe_{3.5}Co_{1.5}SiB_2$	5.5174; 10.2464	6.92	0.20	-0.05	761
Fe_4WSiB_2	5.6425; 10.4744	7.75	0.22	0.218	747
$Fe_{3.35}Co_{1.5}W_{0.15}SiB_2$	5.5505; 10.2413	6.35	0.187	-0.05	638
$Fe_{3.25}Co_{1.5}W_{0.25}SiB_2$	5.559; 10.255	6.70	0.20	-0.055	509
$Fe_{3.5}CoW_{0.5}SiB_2$	5.59 ;10.33	6.88	0.20	-0.038	545
$Fe_{3.0}Co_{1.5}W_{0.5}SiB_2$	5.5834; 10.29	6.14	0.20	0.024	408
$Fe_{2.0}Co_{2.0}WSiB_2$	5.63; 10.32	4.81	0.18	0.105	210
$Fe_{3.0}CoWSiB_2$	5.6376; 10.3942	6.28	0.20	0.067	414

As can be seen in Table 1, Co doping in Fe_5SiB_2 reduces the total magnetic moment and the Curie temperature of the alloys, as shown in our previous experimental and theoretical investigations [2]. Also, Co doping up to y = 1.5 reduces the absolute

value of the anisotropy constant K_1 to -0.05 meV/f.u.. On the other hand, by W for Fe substitution the anisotropy is turning to axial in Fe_4WSiB_2 with K_1 value of 0.218 meV/f.u, corresponding to 0.22 MJ/m^3. This improved anisotropy is accompanied by a decrease of total magnetic moment (8.97 μ_B/f.u.) and a lower Curie temperature (747 K). If the W doping is performed in the $Fe_{3.5}Co_{1.5}SiB_2$ alloy which has small negative value of K_1, the anisotropy is negative up to y = 0.5. Unfortunately, increasing the W content with x > 0.5 in $Fe_{5-x-y}Co_yW_xSiB_2$ (y = 1.0, 1.5 and 2.0) would induce a strong decrease of T_c.

For $Fe_{2.0}Co_{2.0}WSiB_2$ which has axial anisotropy (K_1 = 0.105 meV/f.u.), the Curie temperature is under room temperature and in this way, the obtained magnet would not be able to operate in a reasonable temperature range. In conclusion, the theoretical study proposes Fe_4WSiB_2 alloy as possible candidate for permanent magnet applications due to its increased anisotropy and relatively high values of Curie temperature and total magnetic moment.

The XRD patterns for the $Fe_{5-x}W_xSiB_2$ alloys (x=0.1, 0.2, 0.5 and 1.0) presented in Fig. 1 show the presence of tetragonal phase (*I4/mcm* space group) in all obtained samples. However, for higher W content (x > 0.5) one can see a mixture of phases within the samples. Also, the thermomagnetic measurements found no trace of free Fe in all samples. The lattice constants obtained by refining the XRD patterns from Fig. 1 are shown in Table 2.

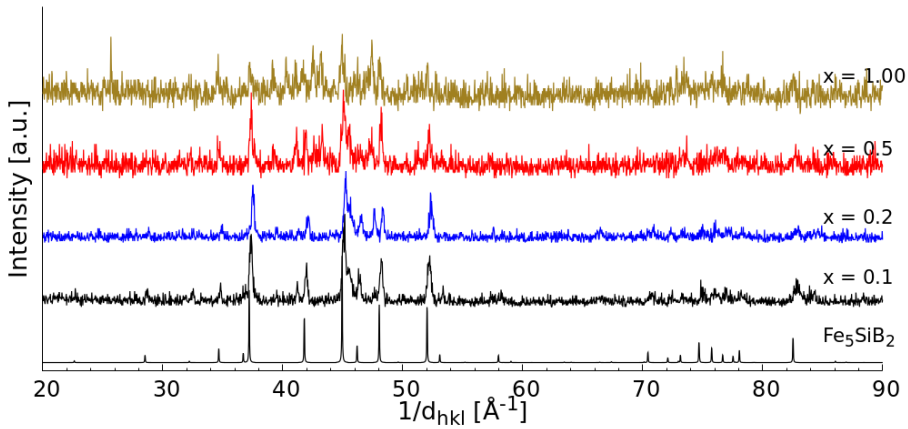


Fig. 1. The XRD patterns for the $Fe_{5-x}W_xSiB_2$ alloys (x=0.1, 0.2, 0.5 and 1.0). The computed XRD pattern for Fe_5SiB_2 is shown for comparison.

Table 2. Lattice constants determined experimentally for the $Fe_{5-x}W_xSiB_2$ alloys

x	Lattice constants (Å)	
	a	c
0.1	5.54(2)	10.31(2)
0.2	5.53(2)	10.28(2)
0.5	5.52(2)	10.26(2)
1.0	5.54(2)	10.37(2)

The thermomagnetic measurements for the $Fe_{5-x}W_xSiB_2$ alloys by heating (a) and by cooling (b) are shown in Fig. 2. By heating, the presence of three different magnetic phases can be evidenced, whilst by cooling only two magnetic phases are present. One of them is the Fe_5SiB_2 phase type with Curie temperatures between 768 (for x = 0.5) and 850 K (for x = 0.1) and the other is a magnetic impurity phase with Curie temperatures between 503 and 553 K, as can be seen in Fig. 2b and Fig. 3.

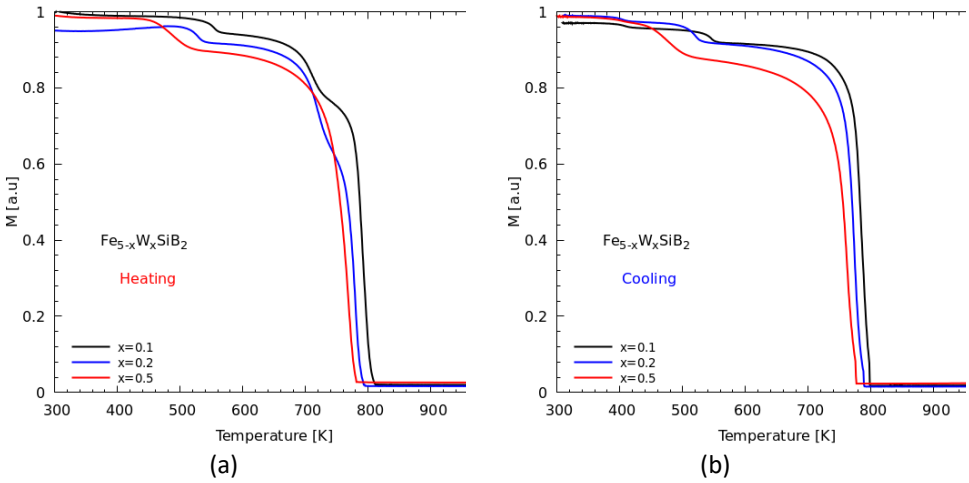


Fig. 2. Temperature dependence of the magnetization for the $Fe_{5-x}W_xSiB_2$ alloys by (a) heating and (b) cooling of the samples.

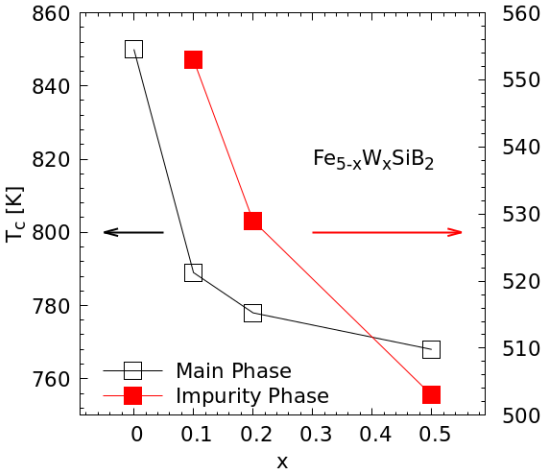
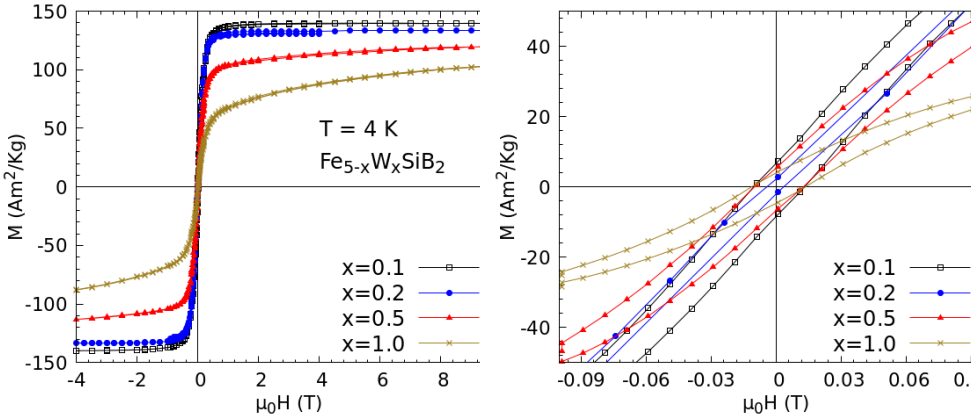


Fig. 3. Composition dependence of the Curie temperatures for the $Fe_{5-x}W_xSiB_2$ alloys. The Curie temperatures of the impurity sample are shown by full squares.



(a) **(b)**

Fig.4. (a) Magnetic hysterezis curves measured at 4 K for the $Fe_{5-x}W_xSiB_2$ alloy and (b) hysterezis curves around the origin for the same system.

The Curie temperatures evolution vs. W content x (Fig. 3) shows that both phases contain Fe and W. The partial substitution of Fe with W reduces the Curie temperature of the corresponding Fe_5SiB_2-doped phases. Accounting for the Curie temperature evolution in the Fe-Si phases [16], the impurity phase is supposed to be the solid solution of Si+W in Fe (α_1 phase).

The hysterezis curves obtained by magnetic measurements (Fig. 4) show a fast saturation of the samples with low W content as well as an anisotropy increase by increasing the W content x. The details of the hysterezis curves around the origin show a low coercivity of the measured samples. Magnetic measurements of the alligned mono-domanines samples would offer a better image on the sample coercivity. Also, the improvement of the present study is intended by using more complex preparation methods, by mechanical alloying or fast cooled ribbons, in order to diminish the impurity phases percentage.

CONCLUSIONS

Theoretical studies on the $Fe_{5-x-y}Co_yW_xSiB_2$ alloys show the decrease of total magnetic moment and Curie temperatures of the alloys by increasing W content x. Also, the theoretical calculated MAE turns from planar for Fe_5SiB_2 alloy to axial for Fe_4WSiB_2 and for $Fe_{5-x-y}Co_yW_xSiB_2$ alloys with W content $x > 0.5$. The experimental investigations show that the samples are mixed phases for magnetic alloys of interest (axial anisotropy, $x > 0.5$). The experimental measured magnetizations and Curie temperatures show agreement with the corresponding theoretical calculations. The improvement of intrinsic magnetic properties for Fe_5SiB_2 alloys by W doping in the investigated doping range is reduced due to the phase mixture appearance. Still, the intrinsic properties of the W doped $Fe_{5-y}Co_ySiB_2$ alloys might be improved by reduction of the impurity phase, which can be obtained using more complex preparation methods.

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