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The magnetization and magnetic anisotropy of iron-rich Fe-W and W-Co intermetallics and nanostructures are investigated by first-principle calculations. The W atom is antiferromagnetically coupled to nearest neighbor Co atom and interface Fe atom in the case of Fe-W multilayers. The first anisotropy constants are positive, nearly zero, or negative, depending on the atomic structures. Typical anisotropy energies per atom are -0.513 meV for a dilute W-Co alloy, -0.06 meV for W_2Fe_2, and 0.44 meV for W_2Fe_4 ($0.1\ \mathrm{meV/atom} \sim 1\ \mathrm{MJ/m^3}$). These values are of interest for permanent-magnet applications but also indicate the need for careful structural control and for a more detailed investigation of structure-property relationships in Fe-W nanostructures.

***Index Terms*—Anisotropy, transition-metal alloys.**

I. Introduction

ELEMENT-STRATEGIC considerations have sparked a renewed interest in rare-earth-free permanent magnets, based entirely on transition-metal elements. The main reason is the rapid industrial growth in the world's main rare-earth producer China and the accompanying uncertainty concerning rare-earth exports [1]. The development and improvement of rare-earth free permanent magnets has remained a long-standing and complicated task [2], [3]. On the one hand, it is difficult to compete against high-end intermetallics such as $Nd_2Fe_{14}B$ [4], $SmCo_5$ [5], and $Sm_2Fe_{17}N_3$ [6]. On the other hand, the raw-materials costs of mass-produced $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ are difficult to beat [3].

To ensure high magnetization and high Curie temperature, it is necessary to use a large fraction of late iron-series elements, but the realization of magnetocrystalline anisotropy (MCA) is then a challenge [2], [3]. Heavy transition metals such as Pd and Pt improve the anisotropy in suitable structures, such as $L1_0$ magnets, but are very expensive. Therefore $3d/4d$ and $3d/5d$ structures are viable route to tune the magnetization and the anisotropy energy. Magnetic anisotropy of Pd and Pt atom in hcp Co host has been studied using first principle calculations [7].

The purpose of this paper is to explore the magnetization and anisotropy of some alloys with *tungsten* as the heavy alloying element. Equilibrium phase diagrams involving W are well-investigated, but progress in experimental nanotechnology makes it possible to fabricate and investigate structures that were not considered in the past. For example, electronic structure calculations indicate a strong orbital moment in some (011)-oriented Fe-W films [8]. The effect depends on the thicknesses of the Fe and W layers, indicating that the nanostructure is important for the understanding of the W anisotropy. Kikuchi *et al.* studied the effects of $5d$ transition elements (X = W, Re, Ir and Pt) on the magnetocrystalline anisotropy of epitaxially grown hexagonal-close-packed Co-X alloys, and reported that magnetic anisotropy energy (MAE) of Co-X significantly changes, depending on X [9]. The magnetic properties of arrays of Fe(110) nanowires grown on W(110) surface has been investigated experimentally [10]. Motivated by these experimental and theoretical finding we investigated the magnetic properties of W atom in hcp Co and $W_2Fe_m(110)$ multilayers.

Our focus is on small concentrations of W atoms in hcp Co hosts and on bcc $W_2Fe_m(110)$ multilayers ($m \leq 4$). It is well-known that MCA is a combined spin-orbit and crystal-field effect [11], but in itinerant magnets, there is a complicated and generally oscillating dependence of anisotropy and orbital moment on chemical composition and atomic structure [12]. Compared to rare-earth anisotropies, the understanding of structure-property relationships for itinerant $3d$, $4d$, and $5d$ anisotropies is poorly developed, and there are no simple rules predicting how atomic substitutions change the anisotropy [12]. It is therefore necessary to perform *ab-initio* calculations, which yield a complicated and generally oscillating dependence of the anisotropy on chemical composition and atomic structure.

II. Numerical Details

The *ab-initio* density functional calculations of the spin moments and magnetic anisotropy of W atom in hcp Co host and $W_2Fe_m(110)$ multilayers ($m \leq 4$) were performed using the VASP code (Vienna *ab initio* simulation package) [13] within the generalized gradient approximation (GGA-PBE) [14]. VASP performs an iterative solution of the Kohn-Sham equations within a plane-wave basis. In our calculation we use the accurate frozen-core full-potential projector-augumented-wave method (PAW) [15]. The basis set contained the

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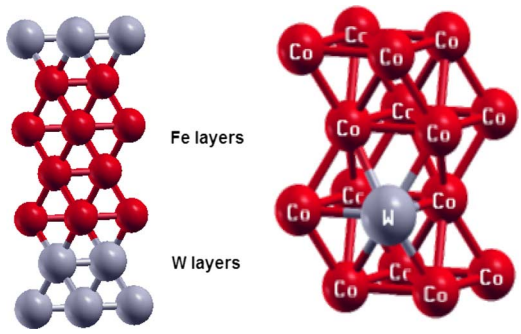

Fig. 1. Atomic structures of the investigated (a) Fe_4W_2 Multilayers structure and (b) W doped Co structure.

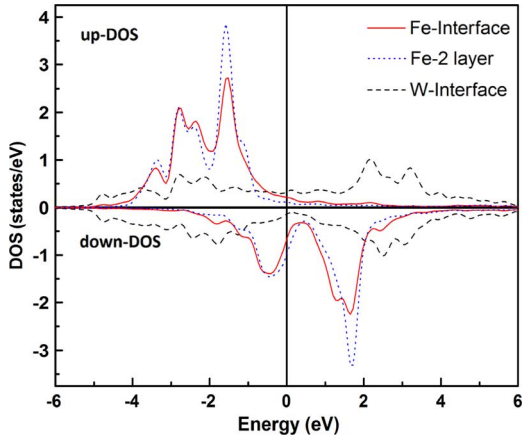

Fig. 2. Typical majority and minority spin-polarized partial densities of states for W2Fe4 multilayers.

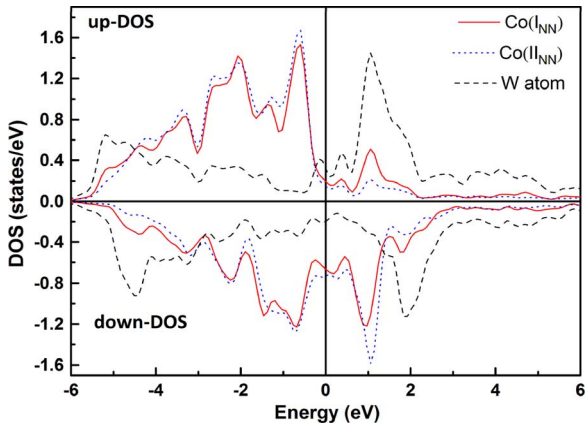

Fig. 3. Typical majority and minority spin-polarized partial densities of states for W atom doped in hcp Co.

plane waves with the maximum kinetic energy of 500 eV for W doped Co and a W_2Fe_m multilayers system, which allows to achieve full basis set convergence. Fig. 1(a), (b) illustrates the investigated W_2Fe_m multilayers and supercell considered in our calculations. One W atom in hcp Co supercell of 16 atoms, corresponds to nominal composition $x = 6.25\%$ or $Co_{15}W$. The lattice constant taken for hcp Co are $a = 2.509$ Å and $c = 8.14$ Å, which corresponding to the interatomic distance of elemental Co, 2.506 Å. The lattice constant used for bcc $W_2Fe_m(110)$ multilayers is 3.19 Å, which is lattice constant of *bcc* W bulk. The magnetic anisotropy and orbital moments are relativistic effects and therefore involve the spin-orbit coupling, which has been implemented in VASP by Kresse and Lebacq [16].

During the relaxation, the first bottom layer of the substrate was frozen in a bulk-like geometry in the case of $W_2Fe_m(110)$ multilayer system and in the case of Co doped W the system is fully relaxed. The structure relaxation is completed after all forces, drop below 0.5 eV/Å. The Brillouin-zone integration has been performed via the Methfessel-Paxton technique [17], on a $13 \times 13 \times 5$ k-points grid for $W_2Fe_m(110)$ and $7 \times 7 \times 7$ k-point grid for Co doped W, using a smearing parameter of 0.2 eV. The calculations have been performed in two steps. First, the scalar-relativistic calculation has been performed for structure relaxation to determine the correct geometry. Then the spin-orbit coupling was included and total energy of the system was determined as a function of orientation of magnetic moments. The magnetic anisotropy energy is computed as the difference between the in-plane and out-of-plane total energy values.

III. Results

Our electronic-structure calculations yield the spin-polarized local density of states (LDOS) for $3d$ and $5d$ electrons in the $Co_{1-x}W_x$ and W_2Fe_4 systems and the local magnetic moments. The Fe and Co spin moments are different from the bulk Fe, because there is a strong hybridization between the Fe or Co $3d$ and W $5d$ electrons. In both cases the majority-spin $3d$ band is almost completely filled. Fig. 2 and Fig. 3 shows the spin-polarized local density of states (LDOS) of d band of W_2Fe_4 multilayer system and W atom doped in hcp Co respectively. The W atom is antiferromagnetically coupled to both Fe and Co atoms. The Fe moment at the Fe-W interface is about 2.6 μ_B for W_2Fe_m, corresponding to an enhancement of 16% compared to the bulk. Table I summarizes the spin and orbital magnetic moments including spin-orbit coupling for in-plane and perpendicular magnetization orientations. The moments of the first- and second-nearest Co neighbors to the W atoms are 1.106 μ_B and 1.380 μ_B, respectively. In W_2Fe_4, the magnetic moment of the second layer of Fe is larger than that of the Fe atoms at the interface. We find that the magnetic moment of the tungsten is antiparallel to the $3d$ magnetization, corresponding to antiferromagnetic (AFM) intersublattice coupling. This is not surprising, because W is an early $5d$ element. However, the W moment in W_2Fe_m multilayers is relatively small, of the order of -0.15 μ_B per atom, so that the magnetization difference between ferromagnetic (FM) and AFM structures is relatively small. An exception is $Co_{1-x}W_x$, where the magnetic moment per W atom is -0.15 μ_B. In practice, this means that the net W content must be kept small to maintain an appreciable magnetization.

The second part of our calculations is concerned with the first anisotropy constant K_1, defined with respect to the main symmetry axis (c-axis) of the systems. The anisotropies are measured in meV per atom, which roughly corresponds to 1 MJ/m^3. There are two basic contributions to the magnetic anisotropy energy. One contribution is the dipole-dipole interaction, which leads to the magnetic shape anisotropy. The other contribution to the magnetic anisotropy is the MCA,

TABLE I
SPIN AND ORBITAL MAGNETIC MOMENT IN (μ_B) OF W_2Fe_m MULTILAYERS SYSTEM AND W DOPED Co SYSTEM

System		Including SOC			
		In-plane		Perpendicular	
		μ_s	μ_l	μ_s	μ_l
W_2Fe_2	W	-0.153	-0.008	-0.153	-0.006
	Fe(*I*)	2.666	0.120	2.664	0.090
W_2Fe_4	W	-0.165	-0.009	-0.167	-0.005
	Fe(*I*)	2.659	0.114	2.658	0.085
	Fe(*I-1*)	2.860	0.074	2.854	0.070
Co doped W	W	-0.505	-0.005	-0.505	-0.013
	$Co(I_{NN})$	1.076	0.050	1.076	0.044
	$Co(II_{NN})$	1.377	0.063	1.378	0.065

which is caused by the spin-orbit coupling of the electrons in magnetic materials [3]. The MCA directly included in the electronic structure and there sum represents our calculated MAE, which is defined as the difference in total energy between the perpendicular and in-plane axis. The W anisotropy is relatively large, of the order of 0.2 meV per atom, but its sign is positive or negative, depending on the W environment. The calculated magnetic anisotropy energy is converged with number of k-points. For W atom doped in hcp the convergence in achieved with 1331 k-points in irreducible brillouin zone and for W_2Fe_m multilayers the convergence in achieved for 845 k-points in irreducible brillouin zone. The small fraction of W atoms, namely $x = 6.25\%$ in hcp Co, leads to change in the orientation of magnetization from perpendicular to in-plane direction, and the value of magnetic anisotropy energy is -0.51 meV. This results agree the previous experimental results in which the magnetic anisotropy of $5d$ transition metal and Co based alloys depends on the concentration of $5d$ transition metal in hcp Co. For W_2Fe_m, the anisotropy energy is -0.06 meV, corresponding to a preferential magnetization axis in the basal plane of the structure. For W_2Fe_4, the calculation yields an anisotropy of $+0.44$ meV and the magnetization is perpendicular to the plane of the structure. Fig. 4. shows the difference in partial density of states for perpendicular and in-plane orientation of magnetization of Fe interface atom. As shown in Fig. 4 it is clear that dominant contribution to MAE is due to $d_{x^2-y^2}$. The W anisotropy contributions of varying sign are consistent with earlier orbital-moment [8] and anisotropy [12] estimates in other itinerant systems and indicate that nanostructuring using W leads to both opportunities and challenges in permanent magnetism research.

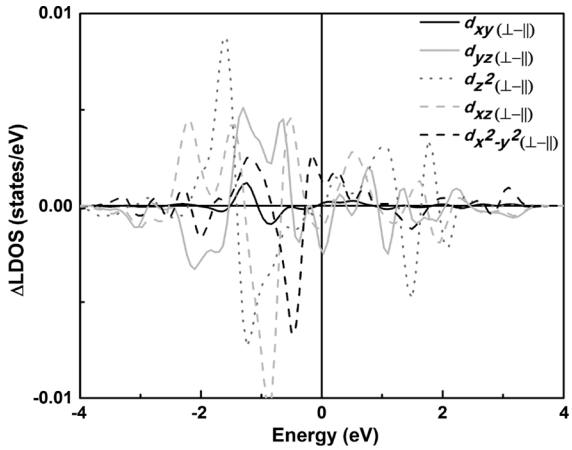

Fig. 4. Differences in partial density of states for Fe interface atom as a function of direction of magnetization.

IV. DISCUSSION AND CONCLUSION

The reason for focusing on W, as contrasted to later $4d/5d$ elements, such as Pd and Pt, is the comparatively low raw-materials price of tungsten. Aside from the ongoing search for magnetic anisotropy in Fe-W based alloys and nanostructures, there is the concern that the W moment couples antiferromagnetic to the Fe sublattice. This feature is expected for alloys between early and late transition metals [3] but negatively affects the net magnetization and the energy product. However, the W moment is rather small and does have a very negative effect on the magnetization if the W content is kept low. Note that this moment reduction is unrelated the anisotropy, which can be positive or negative for both FM and AFM intersublattice couplings.

The present results are promising in the sense that W in Fe and Co creates substantial though not necessarily huge anisotropies. However, the sign and the magnitude of the anisotropy strongly varies from structure to structure. This calls for a further exploration of $3d-4d/5d$ structures rich in Fe, Co, and possibly Mn. Both alloys and nanostructures are of interest in this context.

In conclusion, we have determined the first anisotropy constants of some Fe-W and Co-W structures. The anisotropy constants strongly vary as a function of the structure and composition and even changes sign, but the obtained values are of interest in permanent magnetism. There is reason for cautious optimism that some of these structures may develop into useful permanent magnets.

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