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### Magnetocrystalline anisotropy in YCo<sub>5</sub> and ZrCo<sub>5</sub> compounds from first-principles real-space pseudopotentials calculations

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We investigate the magnetocrystalline anisotropy of YCo<sub>5</sub> and ZrCo<sub>5</sub> compounds from firstprincipes calculations using a real-space formalism of pseudopotentials. We study not only the experimentally observed phases but also other possible crystal structures in order to examine the impact of structural differences on the magnetic properties. Our results indicate that it may be difficult to enhance magnetocrystalline anisotropy constant  $K_1$  and saturation magnetization  $M_s$ simultaneously in YCo<sub>5</sub> compounds in a hexagonal crystal family. We find that ZrCo<sub>5</sub> compounds have moderate  $K_1$  and sufficient  $M_s$ , which can be much better than those of conventional ferrite magnets. We expect that ZrCo<sub>5</sub> compounds, consisting of affordable elements, are promising rareearth-free materials to be useful for permanent magnet applications.

#### I. INTRODUCTION

Magnetocrystalline anisotropy arising from spin-orbit interactions is an indispensable magnetic property for permanent magnets. High magnetocrystalline anisotropy often leads to a large magnetic coercivity that is highly beneficial to yielding a large maximum energy product, which is the product of the magnetic flux density, B, and the magnetic field, H, in a magnetic hysteresis loop,  $[(BH)_{max}]$ . The maximum energy product is a standard measure for the performance of a permanent magnet.<sup>1</sup>

Owing to the spin-orbit interactions, magnetic materials have energetically favorable ("easy") and unfavorable ("hard") directions for the orientation of magnetic moments  $(\vec{m})$ . For a hexagonal crystal structure, the magnetocrystalline anisotropy energy can be expressed as a power series:

$$E(\theta) = K_1 V \sin^2 \theta + K_2 V \sin^4 \theta, \qquad (1)$$

where  $\theta$  is a polar angle measured from the easy axis and V is the volume of a system. The coefficients  $K_1$ and  $K_2$  are the magnetocrystalline anisotropy constants. Suppose the easy axis is along the crystallographic c axis, the magnetic anisotropy energy  $E_a$  can be given by the total-energy difference between the systems magnetized along the easy and hard axes:

$$E_a = E(\vec{m} \perp \vec{c}) - E(\vec{m} \parallel \vec{c}). \tag{2}$$

For most magnetic materials the fourth order constant  $K_2$  is quite smaller than the second order constant  $K_1$  and can be neglected. In this approximation, we can obtain the second order constant  $K_1$  through the relation  $K_1 = E_a/V$ .

In typical rare-earth permanent magnets such those consisting of Nd–Fe–B and Sm–Co, the f electrons of

rare-earth elements play an important role in producing high magnetocrystalline anisotropy in these magnets. For example, SmCo<sub>5</sub> compound has a large magnetocrystalline anisotropy constant  $K_1$  of 17 MJ/m<sup>3</sup>, which is equivalent to a magnetic anisotropy energy  $E_a$  of 16 meV per SmCo<sub>5</sub> formula unit.<sup>2</sup>

There are concerns about available supplies of rareearth elements such as Nd, Sm, and Dy, along with environmental issues with obtaining rare-earth elements. To address these potential supply issues coupled with growing demands for permanent magnets, notable effort has been made in recent years.<sup>3</sup> In the search for a new rare-earth-free magnetic material, Co-based compounds are promising candidate materials that have great potential to exhibit both high magnetization and high magnetocrystalline anisotropy without the presence of felectron ions.

Among the existing rare-earth-free Co-rich magnets, high magnetocrystalline anisotropy has been discovered in an Y-doped Co compound. The YCo<sub>5</sub> compound crystallized in a CaCu<sub>5</sub>-type (P6/mmm) structure has a magnetocrystalline anisotropy constant  $K_1$  of 6.5 MJ/m<sup>3</sup> (equivalently, magnetic anisotropy energy  $E_a$  of 3.4 meV per  $YCo_5$ ).<sup>1</sup> This value is one order of magnitude larger than the value of pure Co bulk ( $K_1 = 0.47 \text{ MJ/m}^3$ , or  $E_a = 0.065$  meV per Co atom).<sup>4</sup> Several theoretical calculations of the magnetic anisotropy energy of YCo<sub>5</sub> have been reported thus far.<sup>5–7</sup> However, previous calculations have been limited to the experimental P6/mmm structure. Magnetic anisotropy is expected to be sensitive to a crystal structure due to coupling of the magnetic moments at each atomic sites with the crystal electric field through the spin-orbit interactions. In spite of its potential importance, magnetic anisotropy in YCo<sub>5</sub> structures has not been explored with respect to the impact of the crystal structure. In addition to an Y–Co system, Zr–Co

compounds<sup>8</sup> are also likely to be a candidate rare-earthfree material that can provide strong magnetocrystalline anisotropy with high magnetization. The natural abundance of Zr is a clear advantage over the scarcity of Y when considering mass production.

We study the magnetocrystalline anisotropy of YCo<sub>5</sub> and ZrCo<sub>5</sub> compounds from first principles. We employ a real-space pseudopotential method to incorporate spin-orbit effects, which are crucial to magnetocrystalline anisotropy. We examine YCo<sub>5</sub> and ZrCo<sub>5</sub> compounds in several crystal structures to assess their potentials for a possible magnetic material with high magnetization and high magnetocrystalline anisotropy. We show that ZrCo<sub>5</sub> compounds can provide moderate magnetocrystalline anisotropy and sufficient saturation magnetization that are good enough for permanent magnet applications.

#### **II. COMPUTATIONAL METHODS**

We employ a real-space formalism of pseudopotentials to compute the magnetic anisotropy energy (Eq. 2). The formalism, implemented in the PARSEC code,<sup>9-11</sup> is designed to obtain the self-consistent solution to the Kohn-Sham equations generalized for the charge density  $n(\vec{r})$ and the spin density  $\vec{m}(\vec{r})$  in the presence of the spin-orbit interactions. We use a generalized-gradient approximation (GGA) functional parametrized by Perdew, Burke, and Ernzerhof (PBE)<sup>12</sup> for the exchange-correlation potential. The spin-orbit interactions are incorporated by norm-conserving pseudopotentials.<sup>13,14</sup> We use a grid spacing of 0.3 a.u. (approximately 0.16 Å), which is fine enough for materials containing 3d transition metals.<sup>15</sup> Pseudopotentials are constructed with the core radii as follows:  $r_s = 2.18, r_p = 2.38$ , and  $r_d = 2.18$  a.u. for Co;  $r_s = 3.19$ ,  $r_p = 3.64$ , and  $r_d = 3.19$  a.u. for Y; and  $r_s = 2.82, r_p = 3.04$ , and  $r_d = 2.82$  a.u. for Zr. (1 a.u. = 0.529 Å.) A partial core correction<sup>16</sup> is included as well. The Monkhorst–Pack scheme<sup>17</sup> is used to generate a kpoint grid to perform Brillouin-zone integration.

#### **III. RESULTS AND DISCUSSION**

#### A. Possible crystal structures

We introduce five crystal structures to be examined as possible structures for YCo<sub>5</sub> and ZrCo<sub>5</sub> compounds. These five structures cover all the XCo<sub>5</sub> structures (X represents any other element) available in the literature<sup>8,18,19</sup> including the experimentally observed phases: (i) The crystal structure with a space group P6/mmm (No. 191) is the experimental structure of YCo<sub>5</sub> and SmCo<sub>5</sub>. The unit cell of the P6/mmmYCo<sub>5</sub> contains five Co atoms that are at two different Wyckoff sites, i.e., Co(2c) and Co(3g), as shown in Fig. 1(a). We will examine P6/mmm ZrCo<sub>5</sub> structure. (ii–iii) Crystal structures with space group R32 (No. 155) and  $P\overline{6}2c$  (No. 190) are reported in an experimentaltheoretical joint study for Zr–Co compounds.<sup>8</sup> As indicated in Fig. 1(b), the R32 YCo<sub>5</sub> phase has four Wyckoff sites for Co atoms. Two of them have six-fold multiplicity and the other two have nine-fold multiplicity. In the  $P\overline{6}2c$  phase, twenty Co atoms are separated into four Wyckoff sites [Co(4e), Co(4f), Co(6g) and Co(6h)] as shown in Fig. 1(c). (iv) The crystal structure with a space group  $P6_322$  (No. 182) comes from a meta-stable phase of  $Sm_4Al_{20}$  compound.<sup>19</sup> The  $P6_322$  YCo<sub>5</sub> phase, shown in Fig. 1(d), has four Wyckoff sites for Co atoms. (v) The R3m (No. 160) structure is a derivative of PuNi<sub>3</sub> structure which possesses a  $R\overline{3}m$  (No. 166) symmetry.<sup>20</sup> As illustrated in Fig. 1(e), two thirds of the original Pu positions are occupied by Y atoms in R3m YCo<sub>5</sub> compound. Co atoms locate at the remaining one third of the original Pu sites as well as at the original Ni sites, leading to crystal symmetry lowering. As a result, the Y sites break into two Wyckoff sites and the Co sites split into six Wyckoff sites.

As in the case of P6/mmm YCo<sub>5</sub>, the crystallographic c axis is chosen to be the z axis for above hexagonal and trigonal XCo<sub>5</sub> structures (X=Y, Zr).

#### B. YCo<sub>5</sub> structures

In Table I, we list the lattice constants of five noncubic YCo<sub>5</sub> structures and their magnetic properties calculated by the real-space method. We find that structural differences in YCo<sub>5</sub> compounds have a small impact on their total magnetic moments. A smaller total magnetic moment is obtained for the R32,  $P6_322$ . and  $P\overline{6}2c$  structures. This is partially due to shortened Co-Co distances. In terms of the magnetic polarization saturation  $\mu_0 M_s$ , where volume effects are renormalized, five YCo<sub>5</sub> structures have practically the same magnetization. Their  $\mu_0 M_s$  values are also comparable to the experimental value of P6/mmm YCo<sub>5</sub>. From the real-space calculations, we obtain positive values of magnetic anisotropy energies for all the hexagonal and trigonal structures of  $YCo_5$ . This means that the easy magnetization axis is aligned along the crystallographic caxis. The P6/mmm YCo<sub>5</sub>, an experimentally observed phase, is predicted to have the largest  $E_a$  among the five structures examined. The R3m YCo<sub>5</sub> structure is predicted to have the largest magnetization among others, while its magnetic anisotropy is found to be largely suppressed. This trend holds for other YCo<sub>5</sub> structures. The present results indicate that it may be difficult to enhance magnetic anisotropy and magnetization simultaneously in  $YCo_5$  compounds in hexagonal crystals.

The calculated  $E_a$  values of YCo<sub>5</sub> compounds are of the order of 1 meV per formula unit. Such a small energy can be sensitive to subtle differences in electronic structure. In order to confirm real-space DFT results, we also performed first-principle DFT calculations by using the projector-augmented wave pseudopotential method<sup>21,22</sup>



FIG. 1: Five non-cubic structures for YCo<sub>5</sub> and ZrCo<sub>5</sub> compounds: (a) P6/mmm (space group No. 191), (b) R32 (No. 155), (c)  $P\overline{6}2c$  (No. 190), (d)  $P6_322$  (No. 182), and (e) R3m (No. 160) structures. Atomic sites labelled X are occupied by Y or Zr atoms. Since the Co sites are inequivalent, we categorize them in six groups, as indicated by different colors.

TABLE I: Lattice parameters of seven XCo<sub>5</sub> compounds (X=Y, Zr) and their magnetic properties calculated by using the real-space pseudopotential DFT code PARSEC: total magnetic moment M ( $\mu_B$  per XCo<sub>5</sub>), magnetic polarization saturation  $\mu_0 M_s$  (T), magnetic anisotropy energy  $E_a$  (meV per XCo<sub>5</sub>), magnetocrystalline anisotropy constant  $K_1$  (MJ/m<sup>3</sup>), and magnetic hardness parameter  $\kappa = \sqrt{K_1/(\mu_0 M_s^2)}$ . The values in brackets are the experimental values of P6/mmm YCo<sub>5</sub>.

		Lattice parameters		Magnetic properties				
Space group		a (Å)	c/a	M	$\mu_0 M_s$	$E_a$	$K_1$	$\kappa$
Trigonal YC	<b>O</b> 5							
R32	(No. 155)	4.80	5.01	6.90	1.00	0.68	1.35	1.30
R3m	(No. 160)	4.87	4.90	7.12	1.02	0.32	0.62	0.87
Hexagonal Y	$Co_5$							
$P6_{3}22$	(No. 182)	4.81	3.34	6.88	1.00	0.68	1.35	1.30
$P\overline{6}2c$	(No. 190)	4.81	3.33	6.88	1.00	0.75	1.50	1.38
P6/mmm	(No. 191)	4.92	0.80	7.13	1.01	1.38	2.68	1.83
		[4.93]	[0.81]		[1.06]		[6.5]	[2.7]
Hexagonal Z	$\mathbf{rCo}_5$							
$P\overline{6}2c$	(No. 190)	4.65	3.44	6.02	0.93	0.59	1.25	1.34
P6/mmm	(No. 191)	4.76	0.83	6.45	0.97	0.49	1.01	1.16

as implemented in the VASP code.<sup>23,24</sup> As in the realspace calculations, a GGA–PBE functional is used. Wave functions are expanded in a plane-wave basis set with a kinetic energy cutoff of 400 eV.

In Fig. 2, the real-space results are compared with the plane-wave results for magnetocrystalline anisotropy constants  $K_1$  of YCo<sub>5</sub> compounds with different crystal structures. Results from the two methods agree well. The difference in  $K_1$  between two methods is about  $0.2 \text{ MJ/m}^3$ . It is much smaller than the absolute value of the experimental  $K_1$  of 6.5 MJ/m<sup>3</sup> in the P6/mmm YCo<sub>5</sub> compound. The  $K_1$  difference of  $0.2 \text{ MJ/m}^3$  corresponds to a total-energy difference of about 0.1 meV per YCo<sub>5</sub>.

#### C. ZrCo<sub>5</sub> structures

In order to investigate the influence of Zr-substitution on the magnetic properties, we apply our real-space method to ZrCo<sub>5</sub> compounds in the P6/mmm [Fig. 1(a)] and  $P\overline{6}2c$  [Fig. 1(c)] structures. The former structure is found in various XCo<sub>5</sub> compounds.<sup>18</sup> It is also the experimental structure of YCo<sub>5</sub> and SmCo<sub>5</sub>. The latter structure was discovered for a Zr–Co compound in Ref. 8.

The calculated magnetic properties are listed in Table I. We find that replacing Y by Zr induces a decrease in the total magnetic moment in ZrCo<sub>5</sub> compounds. To analyze this behavior, the total magnetic moments of P6/mmm YCo<sub>5</sub> and P6/mmm ZrCo<sub>5</sub> are decomposed into local components, which are listed in Table II. The reduction



FIG. 2: The magnetocrystalline anisotropy constants  $K_1$  of YCo<sub>5</sub> compounds with different crystal structures, calculated by using the plane-wave DFT code (VASP) and the real-space DFT code (PARSEC). The GGA–PBE functional is used in both plane-wave and real-space calculations.

of the total magnetic moment in P6/mmm ZrCo<sub>5</sub> can be explained by increased antiparallel contribution from Zr atom and a suppressed local moment of Co atom at the 2c site. Although ZrCo<sub>5</sub> compounds have a reduced total magnetic moment, their magnetic polarization saturation  $\mu_0 M_s$  are still comparable to those of YCo<sub>5</sub> compounds. This is due to a smaller unit-cell volume of ZrCo<sub>5</sub> compounds than YCo<sub>5</sub> compounds. As in the case of YCo<sub>5</sub> structures, for both P6/mmm and  $P\overline{6}2c$  ZrCo<sub>5</sub> structures, the easy magnetization axis is predicted to be the crystallographic c axis. We find that two ZrCo<sub>5</sub> structures exhibit moderate magnetocrystalline anisotropy of  $K_1 \approx 1$  MJ/m<sup>3</sup>.

#### D. Magnetic hardness

A dimensionless parameter  $\kappa = \sqrt{K_1/(\mu_0 M_s^2)}$ , called magnetic hardness parameter, is widely used as an empirical criterion for classifying magnetic materials.<sup>1</sup> In particular, parameter  $\kappa$  is an useful indicator to characterize the strength of magnetic anisotropy of a given material with respect to its magnetization. For example, a material with  $\kappa \geq 1$  and moderate magnetization  $(\mu_0 M_s \geq 1 \text{ T})$  has the potential to yield a large energy product. Such a material can possibly be used as a permanent magnet. In fact, RE-based magnetic materials, such as Nd<sub>2</sub>Fe<sub>14</sub>B and Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub>, satisfy these criteria, as can be seen in Fig. 3, where  $K_1$  is plotted as

TABLE II: A local analysis of the total magnetic moments of P6/mmm YCo<sub>5</sub> and P6/mmm ZrCo<sub>5</sub> compounds.

	Magnetic	Magnetic moment ( $\mu_B$ /atom)		
Site	YCo <sub>5</sub>	$ZrCo_5$		
Y or Zr	-0.18	-0.30		
Co(2c)	1.56	1.33		
Co~(3g)	1.58	1.53		
Interstitial	-0.55	-0.50		
Total	7.13	6.45		



FIG. 3: Magnetocrystalline anisotropy constant  $K_1$  versus magnetic polarization saturation  $\mu_0 M_s$  for YCo<sub>5</sub> and ZrCo<sub>5</sub> compounds as well as popular magnetic materials. The curves correspond to magnetic hardness parameter  $\kappa = \sqrt{K_1/(\mu_0 M_s^2)}$  of 1 (solid), 2 (dashed), and 4 (dotted). We note that the present theory underestimates  $K_1$  by a factor of about 2.

a function of  $\mu_0 M_s$  for popular magnetic materials. In Fig. 3, we also plot theoretical values obtained for  $YCo_5$ and  $ZrCo_5$  compounds. For the experimentally observed P6/mmm YCo<sub>5</sub> structure, the present real-space DFT method gives an accurate magnetization. The method, however, underestimates  $K_1$  by a factor of 2.4, leading to a DFT-based  $\kappa$  being underestimated by a factor of 1.5. Other YCo<sub>5</sub> and ZrCo<sub>5</sub> structures, except for R3mYCo<sub>5</sub>, are predicted to have  $\mu_0 M_s \approx 1$  T and  $\kappa \geq 1$ in the DFT level. Specific values of theoretical  $\kappa$  for all YCo<sub>5</sub> and ZrCo<sub>5</sub> compounds can be found in Table I. In the  $K_1 - \mu_0 M_s$  plot (Fig. 3), YCo<sub>5</sub> and ZrCo<sub>5</sub> structures locate between ferrite ( $\mu_0 M_s = 0.48$  T,  $\kappa = 1.35$ ) and  $Nd_2Fe_{14}B$  magnet ( $\mu_0M_s = 1.61$  T,  $\kappa = 1.54$ ), which dominate the permanent magnet market.<sup>25</sup> Our results indicate that the magnetic properties of YCo<sub>5</sub> and ZrCo<sub>5</sub> structures can be much better than ferrite. We expect that the YCo<sub>5</sub> and ZrCo<sub>5</sub> compounds examined here can serve as new, affordable magnetic materials to fill a gap between conventional ferrite magnets and expensive Nd-Fe–B magnets.

#### IV. SUMMARY

We performed first-principles calculations to study the magnetic properties of  $YCo_5$  and  $ZrCo_5$  compounds with several possible crystal structures including the experimentally observed ones. Overall, structural differences have a small impact on magnetization, but it *does* affect magnetic anisotropy significantly. It may be difficult to enhance magnetocrystalline anisotropy and saturation magnetization simultaneously in YCo<sub>5</sub> compounds in a hexagonal crystal family. We found that  $ZrCo_5$  compounds can provide moderate magnetocrystalline anisotropy and sufficient saturation magnetization that are good enough for permanent magnet applications. We propose  $ZrCo_5$  compounds as possible rare-earth-free low-cost magnets to be useful for permanent magnet applications.

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