Role of the Electronic Structure in the Morphotropic Phase

Boundary of $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ Studied by First-principle Calculation

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Abstract

Physically parallel to ferroelectric morphotropic phase boundary, a phase boundary separating two ferromagnetic phases of different crystallographic symmetries was experimentally found in $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ via high-resolution synchrotron X-ray diffraction. However, lack of the theoretical support makes the morphotropic phase boundary in ferromagnetic system debatable. Here, a first-principle calculation was employed to investigate the electronic structure variation during the morphotropic phase transition in $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$. It offers a theoretical basis for the ferromagnetic phase of different crystallographic symmetries in $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$. It also provides an explanation for why morphotropic phase boundary occurs in $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ alloys and offers a serviceable method to search for the morphotropic phase boundary phenomena in other alloys via computational rather than experimental method.

Keywords: $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$, morphotropic phase boundary, first-principle calculation

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Introduction

RM_2 (R: rare-earth element, M: transition metal) with the cubic Laves phase structure have attracted great attention for their variety of magnetic behavior¹⁻³, which is widely used as functional materials in various applications, such as actuators, sensors and transducers. All of them possess very similar lattice parameters⁴ and exhibit a magnetic instability of the 3d-subsystem⁵. Investigation on electronic structure of RM_2 would improve our understanding on their magnetic behavior. With the more results via experimental progress, the theoretical analysis made it possible to understand systematically the influence of the electronic structure on the magnetic properties⁶. A lot of researches⁷⁻¹⁰ have been contributed on the theoretical and experimental investigation of RFe_2 , RCo_2 and RNi_2 . A debate on the phase transition, if is the spin-reorientation transition also a border separating different crystal symmetries, has been continued for recent decades. In 1960s, H. Horner developed the spin-reorientation transition theory to explain the change in the easy axis of magnetization observed in some ferrimagnets, and pointed out that the easy axis of magnetization in RM_2 is the second-order phase transition which occurred without change in the lattice structure¹¹. However, with the development of lattice measurement, when the easy axis of magnetization in RM_2 changed, a structure transition was observed. Recently, Yang¹²⁻¹⁴ has proved that a Morphotropic Phase Boundary (MPB) situation exists in the ferromagnetic system as same as in the ferroelectric system, which reveals that ferrimagnets transitions in RM_2 occur with a change of lattice structure. The progress in this issue provides a deep insight into the nature of a fundamental concept in magnetism and gives a chance to study the transitions associated with electronic structure. As early as 1970s', Bloch¹⁵ has pointed out that the cobalt moment is not intrinsic but induced in the d band by the exchange field to the rare-

earth, the behavior of transition in RCO_2 has related the density of states at the Fermi Level. However, the principle of MPB in $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ alloy is still unclear, and most of the theoretical explanations concerning the underlying mechanism of MPB in $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ alloy were phenomenological studies^{16,17}. Here, we employed the first-principle calculation method to investigate the electronic structure in $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ alloy and offered a theoretical support to the MPB in the ferromagnetic alloy $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$.

Calculation Method

The calculations have been performed on the basis of Density Functional Theory (DFT)^{18,19} with the ab initio total energy program Cambridge Sequential Total Energy Package (CASTEP)²⁰. For the exchange-correlation functional, we chose a local density approximation in the scheme of Ceperley and Alder²¹ parameterized by Perdew and Zunger²² denoted hereby CA-PZ. The spin interpolation was used in this calculation. The self-consistent ground state of the system was determined using a band-by-band conjugate gradient technique to minimize the total energy of the system with respect to plane-wave coefficients. The electronic wave functions were obtained by the All Bands/ Ensemble Density Functional Theory (EDFT) scheme. For each Co atom, the formal spin state with 4 minority spin electrons was used as initial. The core electrons together with the nuclei were described by pseudo-potentials in the framework of the Projector Augmented Wave (PAW)^{23, 24} method. The one-electron Kohn-Sham wavefunctions as well as the charge density were expanded in a plane-wave basis set. The initial crystal structure model of cubic $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ was build according to the previous research of the synchrotron XRD data¹⁴. Then, the Dy atoms in the supercell were gradually replaced and the cell was geometry optimized. In order to optimize the total energy of $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ with Tetragonal symmetry (T Phase), only the

crystal constant c was relaxed, and the other degrees of freedom were frozen (distorted along 001). Similarly, in order to optimize the total energy of $Tb_xDy_{1-x}Co_2$ with rhombohedral symmetry (R Phase), the crystal constant α , β and γ were only relaxed, and the crystal constant a , b and c were fixed (distorted along 111).

Results and Discussion

The model of $DyCo_2$ in Laves phase was built with the lattice constant $7.12 \text{ \AA}^{25,26}$, and $TbCo_2$ in Laves phase with lattice constant $7.25 \text{ \AA}^{27}$. Then, the special spatial symmetry employed on the model in Laves phase was removed, and atoms in fractional coordinate were constrained. The crystal structure model of $Tb_xDy_{1-x}Co_2$ with T phase or R phase was modified from the Laves phase by distorting along (001) or (111) orientation. Figure 1 shows the Laves phase configuration and the density of states (DOS) for $DyCo_2$. The crystal structure of $DyCo_2$ with Laves belongs to space group $Fd-3m$. Dy atom occupies (0, 0, 0) and Co atom occupies (1/8, 1/8, 1/8). In one conventional cell of $DyCo_2$ as shown in Figure 1a, there is equivalence between all the crystallographic sites of the Dy atoms and of the Co atoms. Therefore, we need to calculate the DOS for one Dy site and one Co site. Figure 1a shows the Laves phase configuration (a), and the DOS for $DyCo_2$ (b). In Figure 1a, a conventional cell, a Dy atom with nearest-neighbor Co atoms, a Co atom with nearest- and next-nearest-neighbor Dy atoms are schematically shown. In a primitive cell, Dy atom with nearest-neighbor Co atoms constructs a truncated tetrahedron, as shown in Figure 1a. Co occupies at the vertex. In Laves phase, because the magnetic property of Co atom depends on the exchange field created by the Dy atoms¹, the model of a Co atom with neighbor Dy atoms should be build. The Co atom with nearest- and next-nearest-neighbor Dy atoms constructs a hexahedron, as shown in Figure 1a. The Dy occupies at the vertex. The

calculated majority and minority spin DOS for Dy and Co atoms are shown in Figure 1b, respectively. The Fermi level lies in the intermediate region of the band, which agrees with other report²⁸. The asymmetry between spin up and spin down DOS for Dy and Co atoms indicate that atomic magnetic moment for Dy or Co is non-zero. M. Cyrot and M. Lavagna²⁸ have theoretically investigated the DOS and magnetic properties of RCO_2 , and interpreted that the interaction between Dy and Co is estimated within the molecular field approximation. The Co is magnetic when the exchange field created by the rare-earth makes the d-orbit of Co split. Our calculation indicates that the d-orbit split induce low spin occupation state for Co atom, as shown in Figure 1b.

The crystallographic cell consists of an eight $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ formula unit. The total energies of T phase $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ were calculated with compressing or stretching the c axis of Laves phase, and the total energies of R phase $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ were calculated with altering the crystal constant α , β and γ of Laves phase, synchronously. The total energies of $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ with T phase or R phase were shown in Figure 2. The horizontal coordinate indicates the distortion of c -axis. The positive value reveals the compression, and the negative value reveals the stretch. On the basis of atom configuration of Laves Phase, we investigated the electronic structure of DyCo_2 . Figure 1 shows the Laves phase configuration and the DOS for DyCo_2 . For one stoichiometric cell, twelve Co atoms locate at the vertex of a truncated tetrahedron, and one Dy atom locates at the center. Co atom with nearest- and next-nearest-neighbor Dy atoms constructs a hexahedron. The Dy locates at the vertex. Within the molecular field approximation, the Co is magnetic only if the exchange field created by near rare-earth is larger than 100T^1 . This is realized for any magnetic rare-earth element²⁹. Our calculation demonstrated that the exchanged field created by Dy made Co magnetics, where the majority spin DOS and minority spin DOS for Co d-orbit are asymmetrical, as

shown in Figure 1b. The inset diagram in Figure 1b shows the degeneration and spin occupation of Co d-orbit. Because Co locates inside a hexahedron constructed by neighbor Dy atoms, the degeneration and spin occupation of Co d-orbit would be perturbed by the substitution of neighbor Dy atoms. Therefore, we can investigate the morphotropic phase transition through the electronic structure. Kimura's group³⁰ has developed an ab initio calculation method to investigate the slight change of electronic structure in phase transition, which has been also proved by the experimental observation in the Martensitic phase transition of $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$. Even if the degenerate states of d orbits were not changed, the phase transition would also be predicted by the evolution of binding energy in the case of varying composites.

We calculated the total energy variation of $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ caused by a tetragonal or rhombohedra distortion from the Laves phase. The results for DyCo_2 ($x=0$) were shown in Figure 2a. It is proved that the T phase is energetically favorable for DyCo_2 . As shown in Figure 2a, the Laves phase, which is the parent phase for $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ above T_c , tends to be unstable against tetragonal or rhombohedral distortion. Significantly, DyCo_2 with AMD symmetry (T phase) manifested a favorite structure, when the c-axis was compressed 0.66Å (9.3%, lattice parameters: $a=b=7.12\text{Å}$, $c=6.46\text{Å}$, $\alpha=\beta=\gamma=90^\circ$), as shown in Figure 2a. Comparing to the energy evolution of DyCo_2 with R phase, the T phase is optimal for DyCo_2 . Interestingly, the T phase tends to be unstable against rhombohedral distortion with increasing Tb composition. For TbCo_2 ($x=1$), the minima in the total energy are located at the 86.5° (angle distortion= 3.5° , lattice parameters: $a=b=c=7.25\text{Å}$, $\alpha=\beta=90^\circ$, $\gamma=86.5^\circ$) along the rhombohedra distortion (R-3M), as shown in Figure 2b. Figure 2b shows the total-energy variation of TbCo_2 ($x=1$) caused by the tetragonal or rhombohedra distortion from the Laves phase. The rhombohedra distortion is more energetically favorable than the tetragonal

distortion. The $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ alloy shows the different symmetry at the Dy-rich side and at the Tb-rich side. Table 1 shows the minima in the total energy of DyCo_2 and TbCo_2 with the tetragonal and rhombohedra symmetry. Such a phenomenon has perplexed the researchers for a long time, because Co atoms were ligands, occupying the vertex of a truncated tetrahedron and the spin electronic configuration of f -orbit for Tb or Dy is too complex to be investigated. To clarify this transition and gain further insight into the origin of the MPB observed in $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$, we have investigated the energy position of peak near E_F , which is apparently responsible for the MPB.

Figure 3 shows the total density of states near E_F in the T phase $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ for $x=0.1, 0.2, 0.3, 0.4, 0.5, 0.6$, and in the R phase of $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ for $x=0.7, 0.8, 0.9, 1$, respectively. A peak was found at about 0.6eV below E_F in the DOS of DyCo_2 . The peak in the DOS is predominantly composed of Co sub-orbitals, as pointed out in Figure 1. With an increase in the Tb composition, the peak shifts towards E_F . The peak shift can be attributed to the hybridization between the Co 3d orbitals and 4f orbitals of excess Tb atoms at Dy sites^{31,32}. It should be noted that the magnetic moment of $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$ was offered by Co. The substitute of Dy by Tb only changed the electrostatic potentials, which would affect the energy of Co 3d sub-orbitals. Considering the hybridization between the Co 3d orbitals and 4f orbitals of Tb or Dy, the peak in the DOS would shift towards E_F . Due to the limitation of the degenerate states of Co 3d orbitals, the peak would not shift through the E_F . However, due to the substitute of Dy by Tb, the peak shifts more and more close to the E_F . As a result, the phase boundary was located between the Dy-rich side and the Tb-rich side. Our calculation predicted that such a phase boundary should locate around $x=0.7$ for $\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$. Crossing the phase boundary, the peak would shift away from the E_F , as the composite of Tb increases. Such a calculation results could be simply understood via studying the

relationship between number of valence electrons (NVE) and E_F . However, the peak corresponding to Co 3d orbit is prohibited to cross E_F . Therefore, the phase transition occurs, when the abnormal shift is reversed.

The most interesting feature of the MPB composition is the magneto-responsive properties. Certainly, the MPB would separate two composite dependence free energy evolutions in accordance with symmetry. Figure 4 shows the composition dependence of free energy, integrated spin density and Fermi energy. We calculated the favorite free energy with different mole percent of $Tb_xDy_{1-x}Co_2$. It is clear that near the phase boundary the energetically favorite structure transited from R phase ($x > 0.7$) to T phase ($x < 0.6$). Accompanying the free energy varying, the integrated |spin density| shows a step at the MPB composition, as shown in Figure 4b. The integrated |spin density| denotes the spontaneous magnetization. Figure 4c shows the variation of Fermi level as a function of the composite. It is significant that a transition occurred at the MPB composition. The MPB separated $Tb_xDy_{1-x}Co_2$ into different symmetries.

Conclusions

In conclusion, we studied a magnetic MPB in a ferromagnetic $Tb_xDy_{1-x}Co_2$ system, which separates two magnetic phases with different crystal symmetries. The MPB leads to a significant variation in magnetic properties and in crystal structure. The calculation reveals that the MPB is a boundary of T and R phase and is a thermodynamically bistable states. In the ferromagnetic $Tb_xDy_{1-x}Co_2$ system, the MPB was calculated in the vicinity of $Tb_{(0.5\sim0.6)}DyCo_2$, which is close to the stoichiometry of $Tb_{x\approx0.6}DyCo_2$ at MPB in the experiment¹⁴. Our energetic analysis draw a consistent conclusion with the phenomenological simulation that the phase transition process occurs from

TbCo₂-rich phase to DyCo₂-rich phase. The MPB in ferromagnetic system may provide an effective approach for developing highly magnetostrictive materials, and suggests the possibility of MPB in other ferric systems. The calculation of MPB offers an approach to search the MPB composition. It also makes us deeply understand the nature of magnetism and phase transition.

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Table 1

Alloy	Total energy (eV)		Favorable structure
	Tetragonal	Rhombohedral	
DyCo ₂	$\Delta c=0.66\text{\AA}$	$\Delta\alpha=\Delta\beta=0.7^\circ$	Tetragonal (a=7.12 Å, c=6.46Å)
	-48607.9	-48607.2	
TbCo ₂	$\Delta c=0.33\text{\AA}$	$\Delta\alpha=\Delta\beta=3.5^\circ$	Rhombohedral (a=7.25 Å, $\alpha=86.5^\circ$)
	-44720.9	-44721.1

Figure 1. The Laves phase configuration and the DOS for DyCo₂.

Figure 2. (a). The total energies of DyCo₂ with Tetragonal symmetry and Rhombohedral symmetry.
 (b). The total energies of TbCo₂ with Tetragonal symmetry and Rhombohedral symmetry

Figure 3. The total density of states near E_F , in the tetragonal phase of Tb_xDy_{1-x}Co₂ for x=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and in the rhombohedral phase of Tb_xDy_{1-x}Co₂ for x=0.7, 0.8, 0.9, 1, respectively.

Figure 4. Composition dependence of physical properties in relation with MPB composition. Inset in (b) is the experimentally measured saturation magnetization M_s in relation with MPB composition.

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