Role of Electronic Structure in the Morphotropic Phase Boundary
of Tb$_x$Dy$_{1-x}$Co$_2$ Studied by First-principles Calculation

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Abstract

Physically parallel to ferroelectric morphotropic phase boundary, a phase boundary
separating two ferromagnetic phase of different crystallographic symmetries was found
in Tb$_x$Dy$_{1-x}$Co$_2$. High-resolution synchrotron XRD has been carried out to offer
experimental evidence for Tb$_x$Dy$_{1-x}$Co$_2$. It has been proved that Tb$_x$Dy$_{1-x}$Co$_2$ (0.6<x<0.7)

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is a morphotropic phase boundary and that the crystal structures of tetragonal (x<0.6) and rhombohedral (x>0.7) phase is distorted from a Laves Phase. Here, a first principles calculation provides a theoretical explanation on the origin of MBP in Tb$_x$Dy$_{1-x}$Co$_2$ and is also provided for the question of why MPB occurs in Tb$_x$Dy$_{1-x}$Co$_2$ alloys.
RM$_2$ (R: rare-earth element, M: transition metal) with the cubic Laves phase structure have attracted great attention for their variety of magnetic behavior$^{1-3}$. All of them possess very similar lattice parameters$^4$ and exhibit a magnetic instability of the 3d-subsystem due to the occupation of $d$ and $f$ orbitals$^5$. Investigation on electronic structure of RM$_2$ would improve our understanding on mechanism of their magnetic behavior. With the more results provided by experimental progress, the theoretical analysis made it possible to understand systematically the influence of the electronic structure on the magnetic properties$^6$. A lot of researches$^{7-10}$ have been contributed on the theoretical and experimental investigation of RFe$_2$, RCo$_2$ and RNi$_2$. Especially for Tb$_x$Dy$_{1-x}$Co$_2$, 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. The progress in this issue provides a deep insight into the nature of a fundamental concept in magnetism and provides a chance to study the transitions associated with electronic structure. Specially, the magnetic properties of cobalt are strongly depended on the rare-earth element. It offers an opportunity to investigate the occupation of $d$ and $f$ orbitals and hybridization between them. As early as 1970s’, Bloch$^{11}$ have pointed out that the cobalt moment is not intrinsic but induced in the d band by the exchange field due to the rare-earth, the behavior of transition in RCo$_2$ have related the density of states
at the Fermi Level. Recently, Yang\textsuperscript{12-14} has proved that a similar MPB situation exist in
the ferromagnetic system as same as in the ferroelectric system, which have rectified the
long standing mistake that the magnetic transition in Tb\textsubscript{x}Dy\textsubscript{1-x}Co\textsubscript{2} alloy is merely a
reorientation of magnetization direction and there is no change in crystal symmetry.
This promises to change our perception of how we think about the magnetic theory.
Yang employed the high-resolution synchrotron XRD at the BL15XU NIMS beat line of
Spring-8 to experimentally confirm the transition in Tb\textsubscript{x}Dy\textsubscript{1-x}Co\textsubscript{2} alloy. However, most
of the theoretical explanations concerning the underlying mechanism of MPB have been
phonological studies\textsuperscript{15,16}. In this letter, we investigated the electronic structure at the
Fermi Level in Tb\textsubscript{x}Dy\textsubscript{1-x}Co\textsubscript{2} and clarified the origin of different ferromagnetic states
corresponding to different crystal symmetries in Tb\textsubscript{x}Dy\textsubscript{1-x}Co\textsubscript{2} alloy by using first
principles calculation. This work provides a theoretical explanation on the origin of
MBP in Tb\textsubscript{x}Dy\textsubscript{1-x}Co\textsubscript{2} and is also provided for the question of why MPB occurs in
Tb\textsubscript{x}Dy\textsubscript{1-x}Co\textsubscript{2} alloys.

The calculations have been performed on the basis of spin-polarized DFT\textsuperscript{17,18} with
the \textit{ab initio} total energy program CASTEP\textsuperscript{19}. For the exchange-correlation functional,
we chose a local density approximation in the scheme of Ceperley and Alder\textsuperscript{20}
parameterized by Perdew and Zunger\textsuperscript{21} 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/EDFT scheme. A number of twelve valence
electrons for each Dy atom (4f^{10}6s^2) and eleven valence electrons for each Tb atom
(4f^96s^2) were taken into account. For each Co atom (3d^74s^2), a number of nine valence
electrons were employed and the formal spin state with 4 minority spin electrons was
used as initial. The remaining core electrons together with the nuclei were described by
pseudo-potentials in the framework of the PAW method^22, 23. 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 TB_xDy_{1-x}Co_2 was build according
to the previous research of the synchrotron XRD data^14. Then, the Dy atoms in the
supercell were gradually replaced and the cell was geometry optimized. In order to
optimize the total energy of TB_xDy_{1-x}Co_2 with Tetragonal symmetry, the crystal constant
c was only relaxed, and the other degrees of freedom were frozen. Similarly, in order to
optimize the total energy of Tb_xDy_{1-x}Co_2 with Rhombohedral symmetry, the crystal
constant α, β and γ were only relaxed, and the crystal constant a, b and c were fixed.
The lattice parameters for DyCo_2 and TbCo_2 at 0 K were extrapolated from the low
temperature X-ray analysis. A model of DyCo2 in Laves phase was built with the lattice constant 7.12 Å$^{24,25}$, and TbCo2 in Laves phase with lattice constant 7.25 Å$^{26}$. Then, the special symmetry employed on the model in Laves phase was canceled, and atoms in fractional coordinate were constrained. The crystal structure model of Tb$_x$Dy$_{1-x}$Co$_2$ with tetragonal symmetry or rhombohedral symmetry was modified from the Laves phase. Figure 1 shows the Laves phase configuration and the DOS for DyCo2 with Laves phase. The crystallographic cell consists of an eight Tb$_x$Dy$_{1-x}$Co$_2$ formula unit. The total energies of Tb$_x$Dy$_{1-x}$Co$_2$ with Tetragonal symmetry were calculated with the compressing or stretching the $c$ axis of Laves phase, and the total energies of Tb$_x$Dy$_{1-x}$Co$_2$ with Rhombohedral symmetry were calculated with altering the crystal constant $\alpha, \beta$ and $\gamma$ of Laves phase, synchronously. The $c$-axis was distorted to calculate the total energy of Tb$_x$Dy$_{1-x}$Co$_2$ with AMD symmetry. Otherwise, the angle was distorted to calculate the total energy of Tb$_x$Dy$_{1-x}$Co$_2$ with R-3M symmetry. The total energies of Tb$_x$Dy$_{1-x}$Co$_2$ with Tetragonal symmetry and Rhombohedral symmetry 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. The ground state of the Tb$_x$Dy$_{1-x}$Co$_2$ was determined by considering spin configurations. All magnetic moments are aligned parallel in the ferromagnetic (FM) state for a
crystallographic cell, which is consistent with the FM nature of Tb$_x$Dy$_{1-x}$Co$_2$ under the Curie temperature.

Firstly, 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. The inset diagram is the schematic of spin electron configuration for Co atom in the truncated tetrahedron. In the view of classical crystal field theory, due to the Co’s occupation at the vertex of a truncated tetrahedron rather than the central, the distortion of the crystal structure would not affect the spin electronic configuration of Co. It implies that there would be no structure phase transition in the case of Dy’s substitute by Tb. It is significantly far from the experimental observation and our results of total energy calculation. Prof. Kimura$^{27}$ has developed an *Ab initio* calculation method to investigate the slight change of electronic structure in phase transition, which have been also proved by the experimental observation in the Martensitic phase transition of Ni$_2$Mn$_{1+x}$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 Tb$_x$Dy$_{1-x}$Co$_2$ caused by a tetragonal and
rhombohedra distortion form the Laves phase. The results for DyCo$_2$ (x=0) were shown in Figure 2a. The tetragonal phase is energetically favorable for DyCo$_2$, as reported previously\textsuperscript{14}. As shown in Figure 2a, the Laves phase, which is the parent phase for Tb$_x$Dy$_{1-x}$Co$_2$ above $T_c$, tends to be unstable against tetragonal and rhombohedral distortion at low temperature. Significantly, DyCo$_2$ with tetragonal phase (AMD symmetry) manifested a favorite structure, when the c-axis was compressed 9.3\%. Comparing to the energy evolution of DyCo$_2$ with rhombohedral phase, the tetragonal phase is optimal for DyCo$_2$. Interestingly, the tetragonal phase tends to be unstable against rhombohedral distortion with increasing Tb composition\textsuperscript{26}. For TbCo$_2$ (x=1), the minima in the total energy are located at the 86.5° along the rhombohedra distortion (R-3M). Figure 2b shows the total-energy variation of TbCo$_2$ (x=1) caused by the tetragonal or rhombohedral distortion from the Laves phase. The rhombohedral distortion is more energetically favorable than the tetragonal distortion. The theoretical results are consistent with the experimental observation\textsuperscript{26,28}, where the Tb$_x$Dy$_{1-x}$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 rhombohedral 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 Tb$_x$Dy$_{1-x}$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 tetragonal phase of Tb$_x$Dy$_{1-x}$Co$_2$ for x=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and in the rhombohedral phase of Tb$_x$Dy$_{1-x}$Co$_2$ for x=0.7, 0.8, 0.9, 1, respectively. A peak was found at about 0.6 eV below $E_F$ in the DOS of DyCo$_2$. The peak in the DOS is predominantly composed of Co 3d sub-orbitals, as pointed out in Figure 1. With an increase in the Tb composition, the peak structure 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. It should be noted that the magnetic moment of Tb$_x$Dy$_{1-x}$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, rather than the degenerate states. Comparing to the Dy, Tb lacks a 4f electron. 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

$\text{Tb}_x\text{Dy}_{1-x}\text{Co}_2$, which well agrees the previous experimental observation\textsuperscript{14}. Crossing the
d 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 $E_F$. If the Dy site is

substituted by a Tb atom, a smaller NVE would be expected to result a drop of $E_F$. The

abnormal shift of the peak in the vicinity of $E_F$ is attributed to the variation of NVE.

However, the peak corresponding to Co 3$d$ 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 integrated spin density and Fermi energy. Accompanying the free energy varying, the

integrated $|\text{spin density}|$ shows a step at the MPB composition, as shown in Figure 4a.

The integrated $|\text{spin density}|$ denotes the spontaneous magnetization, which is also

superiority at Tb-rich side in the experimental observation\textsuperscript{14} as shown in the inset of

Figure 4a. Figure 4b 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$_x$Dy$_{1-x}$Co$_2$ into different symmetries.

In conclusion, we proved a magnetic MPB in a ferromagnetic Tb$_x$Dy$_{1-x}$Co$_2$ system, which separates two magnetic phase 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. The proving of MPB in ferromagnetic system may provide an effective approach for developing highly magnetostrictive materials, and suggests the possibility of MPB in other ferroic systems. The calculation of MPB provides an effective approach to search the MPB composition. It also provides a new insight into the nature of magnetism and phase transition.

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29.
Table 1. Comparison of total energy between DyCo$_2$ and TbCo$_2$ with the tetragonal and rhombohedral symmetry

|       | Total energy (eV) | Favorable structure                  |
|-------|------------------|--------------------------------------|
|       | Tetragonal   | Rhombohedral                         |
| DyCo$_2$ | -48607.9    | -48607.2                             | Tetragonal (a=7.12 Å, c=6.46Å)       |
| TbCo$_2$ | -44720.9    | -44721.1                             | Rhombohedral (a=7.25 Å, α=86.5°)     |
Captions

Figure 1. The truncated tetrahedron configuration and the DOS for DyCo$_2$ with Laves phase.

Figure 2. (a). The total energies of DyCo$_2$ with Tetragonal symmetry and Rhombohedral symmetry. (b). The total energies of TbCo$_2$ with Tetragonal symmetry and Rhombohedral symmetry.

Figure 3. The total density of states near $E_F$, in the tetragonal phase of Tb$_x$Dy$_{1-x}$Co$_2$ for $x=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$, and in the rhombohedral phase of Tb$_x$Dy$_{1-x}$Co$_2$ for $x=0.7, 0.8, 0.9, 1$, respectively.

Figure 4. Composition dependence of physical properties in relation with MPB.
Figure 1

Figure 2
Figure 3
Figure 4