A full electron LMTO-ASA study of electronic band structure and magnetic properties for $\text{RFe}_{11}\text{TiN}_x$ ($\text{R}=\text{Y, Nd, Sm}; x=0,1$)

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The band structure and magnetic properties are studied for $\text{RFe}_{11}\text{TiN}_x$ ($\text{R}=\text{Y, Nd, Sm}; x=0,1$) rare-earth iron intermetallic compounds using the linear muffin tin orbital with the atomic sphere approximation (LMTO-ASA) method. In order to elucidate the role played by the rare-earth atoms in these compounds, a full electron calculation is performed using a semirelativistic spin-polarized LMTO-ASA method in the local spin density approximation (LSDA) regime. The 4f electrons of the rare-earth atoms are considered to be valence electrons in the self-consistent calculations. For NdFe$_{11}$TiN, a calculation in which the 4f electrons are treated as core-frozen states is also performed, and is compared with the full electron calculation. The effects of N atoms in these compounds are also discussed.

I. INTRODUCTION

The rare-earth iron ternary intermetallic compounds have attracted great attention as promising new permanent magnetic materials. Theoretical first-principle calculations regarding these materials are few, because of the complexity of these systems and the presence of the rare-earth 4f electrons. In early works, band structure calculations of the electronic structure of these materials often focused on the Y compounds. For instance, Jaswal et al.$^1$ and Sakuma$^2$ have calculated the electronic structure of $\text{Y}_2\text{Fe}_{17}\text{N}_x$ ($x=0.3$) and $\text{YFe}_{11}\text{TiN}_x$ ($x=0.1$), respectively, using the LMTO-ASA band method. Choosing Y rather than the rare-earth atoms avoids the trouble of considering 4f electrons, but these systems differ from the realistic materials that have applied prospects. These results using Y may only provide some qualitative discussion about the rare-earth iron compounds. It is better to perform the electronic structure calculations for realistic systems. Jaswal$^3$ has used a simple method in which the 4f states were treated as frozen-core states for Nd$_2\text{Fe}_{14} \text{B}$. Hummler et al.$^4$ have studied $\text{RFe}_2\text{B}_2$ ($\text{R}=\text{Gd, Tb, Dy, Ho, and Er}$) using a so-called “open core” approximation in which 4f electrons are not allowed to hybridize with other valence electrons. The latter approximate method can only consider the effects on the 4f energy level by the crystal field and the possible hybridization and charge transfer are neglected. Recently, Asano et al.$^5$ have studied the electronic structure of $\text{RFc}_{11}\text{A}$ ($\text{R}=\text{Y, Ce, Gd}; \text{A}=\text{N, C}$), and the 4f electrons were treated as valence electrons. Their results indicate that the calculation of the electronic structure can explain the experimental results in the frame of the Stoner–Wohlfarth theorem. In their work, the role of N or C atoms are not discussed sufficiently. Zeng et al.$^6$ have calculated the electronic structure of $\text{R}_2\text{Fe}_{17}\text{N}_3-\delta$ ($\text{R}=\text{Sm, Nd, and Gd}$; $\delta=0.3$) using the cluster method. Their results imply that there are relatively strong hybridizations between 4f and other valence electrons. Many experiments also show that there exist differences in the properties of R–Fe–A compounds for different rare earths, especially for light rare earths. This difference cannot be attributed to the de Gennes factors completely. Hence, treatment of the 4f electrons as valence electrons in the band calculations is necessary.

In this work, the full-electron self-consistent spin-polarized band calculation for $\text{RFe}_{11}\text{TiN}_x$ ($\text{R}=\text{Y, Nd, and Sm}; x=0,1$) has been performed using the semirelativistic LMTO-ASA method. The frozen core approximation is used for the inner close shells for simplification. The maximum $l$ is taken as $l_{\text{max}}=3$ for R, $l_{\text{max}}=2$ for Y, Fe, Ti, and $l_{\text{max}}=1$ for N. The crystal structure of $\text{RFc}_{11}\text{TiN}_x$ is as shown in Ref. 2 and the lattice parameters are from Refs. 2 and 8. The ratio of the atomic sphere radius is $r_a/r_{\text{Fe}}; r_{\text{Fe}}; r_{\text{Ti}}, r_{\text{N}}=1.23:1.00:1.10$ for $\text{RFc}_{11}\text{Ti}$ and $r_a/r_{\text{Fe}}; r_{\text{Fe}}; r_{\text{Ti}}, r_{\text{N}}=1.40:1.15:1.25:1.00$ for $\text{RFc}_{11}\text{TiN}_x$. As a comparison, a calculation of electronic structure for NdFe$_{11}$TiN is also performed, with the 4f electrons of Nd in a frozen core approximation.

II. RESULTS AND DISCUSSION

A. Magnetic moments

The magnetic moments of R, Fe, and N (for $x=1$) atoms in $\text{RFc}_{11}\text{TiN}_x$ compounds are listed in Table I. In the case of $x=0$, the Fe(8i) atoms have the highest moments and the Fe(8f) atoms have the lowest ones. The average moment for Fe atoms is 2.14$\mu_b$, 2.23$\mu_b$, and 2.15$\mu_b$ for YFe$_{11}$Ti, NdFe$_{11}$Ti, and SmFe$_{11}$Ti, respectively. These results are similar to those of Asano et al.$^5$ for YFe$_{11}$Ti$^5$ and those of Jaswal for NdFe$_{11}$Ti$^5$. The calculated magnetic moments are slightly higher than the experimental values. This discrepancy seems to possess a systematic character and is insensitive to the radius of atomic sphere used in different works. It is interesting to note that the magnetic moments may slightly depend on the number of $k$ points used in the band calculation. There are 126 $k$ points in the irreducible Brillouin zone in our self-consistent calculation, which is smaller than the 215 $k$ points used by Asano et al.$^5$ but larger than the six $k$ points used by Jaswal.$^3$ The calculated total magnetic moments of transition metal atoms are 22.60$\mu_b$, 23.57$\mu_b$, and 22.76$\mu_b$ for YFe$_{11}$Ti, NdFe$_{11}$Ti, and SmFe$_{11}$Ti, respectively. In the LMTO calculation, the nonzero contribution of the orbital moment for rare-earth atoms was not evaluated. Due to the
TABLE I. Calculated local and total magnetic moments (in $\mu_B$/atom and $\mu_B$/f.u., respectively) for RFe$_{11}$TiN$_x$(R=Y, Nd, and Sm; x=0, 1).

<table>
<thead>
<tr>
<th></th>
<th>YFe$_{11}$TiN$_x$</th>
<th>NdFe$_{11}$TiN$_x$</th>
<th>SmFe$_{11}$TiN$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x=0$</td>
<td>$x=1$</td>
<td>$x=0$</td>
</tr>
<tr>
<td>Fe(8f)</td>
<td>-0.84</td>
<td>-0.34</td>
<td>2.23</td>
</tr>
<tr>
<td>Fe(8j)</td>
<td>0.00</td>
<td>0.00</td>
<td>(2.71)</td>
</tr>
<tr>
<td>Fe(8i)</td>
<td>2.54</td>
<td>2.62</td>
<td>2.56</td>
</tr>
<tr>
<td>Ti(8i)</td>
<td>-0.94</td>
<td>-1.02</td>
<td>-0.96</td>
</tr>
<tr>
<td>N(2b)</td>
<td>0.10</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>Fe</td>
<td>0.14</td>
<td>0.37</td>
<td>0.23</td>
</tr>
<tr>
<td>(av.)</td>
<td>(1.69)</td>
<td>(1.98)</td>
<td>(1.69)</td>
</tr>
<tr>
<td>Total</td>
<td>22.14</td>
<td>24.28</td>
<td>26.29</td>
</tr>
</tbody>
</table>

*The bracketed data are experimental data from Ref. 12, f.u. denotes the formula unit, and Fe (aver.) represents the average Fe magnetic moment.

Magnetic anisotropy, the magnetic moments of the rare-earth and iron atoms may be not collinear. In Table I, only the spin moments are listed for the rare-earth atoms. The moment of each Y atom is $-0.42\mu_B$, which comes from the polarization of the 4$d$, 5$s$ electrons. The spin moment of Nd and Sm in RFe$_{11}$Ti is 2.73 $\mu_B$ and 5.19 $\mu_B$, respectively. Due to the neglecting of spin orbit coupling and the orbital moment in our semirelativistic LMTO-ASA calculations, one cannot compare the spin moments directly with experimental magnetic moments of rare-earth ions. However, our calculations will describe the coupling of moments between Fe and rare-earth atoms. The self-consistent calculations reveal a ferromagnetic coupling between the spin of Fe and Nd (or Sm) in Nd (or Sm) Fe$_{11}$Ti compounds. The moment of each Ti atom is $-0.94\mu_B$, $-0.96\mu_B$, and $-0.89\mu_B$ for Y, Nd, and Sm compounds, respectively, which is antiferromagnetically coupled with the Fe moments. This antiferromagnetic coupling between Fe and Ti is similar to that of YFe$_8$T$_4$ discussed by Coehoorn. The magnetic moment of Fe atoms are increased by the uptake of nitrogen, which is in agreement with experiments. The largest Fe moments are still associated with the Fe(8j), but the largest increment of moments are associated with the Fe(8f) atoms, which is 0.55 $\mu_B$, 0.23 $\mu_B$, and 0.28 $\mu_B$ for YFe$_{11}$TiN, NdFe$_{11}$TiN, and SmFe$_{11}$TiN, respectively. The moments of Fe(8j) atoms, which are the nearest neighbors of N atoms, are not changed for YFe$_{11}$TiN, and even show a small reduction for NdFe$_{11}$TiN and SmFe$_{11}$TiN. The moments of Ti are still antiferromagnetically coupled to the Fe sublattice, and have a $\approx0.1\mu_B$ increment. There is a moment of 0.1 $\mu_B$ on N atoms due to the spin polarization of s,p electrons. The average moment of Fe atoms is 2.32 $\mu_B$, 2.34 $\mu_B$, and 2.32 $\mu_B$ for Y, Nd, and Sm compounds, respectively. It seems to be a general trend that the magnetic moment of Fe in iron nitride depends on the distance from neighboring N atoms. The results of Fe$_4$N, Fe$_{15}$N$_2$, R$_2$Fe$_5$N$_3$, and RFe$_{11}$TiN show that the lowest magnetic moment of Fe always corresponds to the nearest neighbor of a N atom. The moments of Nd in Nd compounds and that of Sm in SmFe$_{11}$Ti are ferromagnetically (FM) coupled to the moments of Fe. This coupling becomes antiferromagnetic (AFM) for the SmFe$_{11}$TiN compound. This fact is qualitatively in agreement with the measurement results of Yang et al.\textsuperscript{11}

B. Density of states

The calculated partial density of states (PDOS) of YFe$_{11}$Ti and YFe$_{11}$TiN are similar to that of Sakuma.\textsuperscript{7} After uptaking N, the 3$d$ band of Fe atoms become narrower, due to the increased distance between Fe atoms. The PDOS of majority moment of the 3$d$ band is slightly low, which produces an enhancement of the moment of Fe and a reduction of the DOS at Fermi surface $E_F$. Then the reduction of $N(E_F)$ is responsible for the increase of Tc in these compounds. There is explicit hybridization between 3$d$ of Fe(8j) and N 2$p$ at an energy about 6 eV below $E_F$. The effect of the presence of N atoms is not only changing the crystalline field, but also producing a hybridization between electrons of N, Fe(8j), and Y.

The PDOS of SmFe$_{11}$TiN$_x$ (x=0,1) are shown in Fig. 1. The essential situation is similar to that of Y compounds, except for the PDOS of the rare-earth atoms. These facts confirm that the discussion based on the calculated results of Y compounds can give a qualitatively correct conclusion about magnetic moments. From these figures, the spin polarization of the N 2$p$ band in these magnetic materials is small. The main contribution of the N 2$p$ band is around the energy of $-4.5$--$-8.0$ eV. It is worthwhile to point out that the difference between the full electron and frozen 4$f$ calculation reveals the effect of interaction among the 4$f$ electrons of rare-earth atoms, 3$d$ of Fe(8j), and 2$p$ of N atoms. The hybridization is taking place among not only N 2$p$, Fe(8j) 3$d$ and 4$s$, R(Nd, Sm) 5$d$ and 6$s$, but also 4$f$ of Nd or Sm. It is interesting to point out that, for the case of SmFe$_{11}$TiN, although we begin with a ferromagnetic coupling between moments of R and Fe, the self-consistent calculation gives an antiferromagnetic coupling between Fe sublattice moments and a Sm 4$f$ moment, which is in agreement with the experiments of Yang et al.\textsuperscript{11} It is well known that the spin-orbit...
coupling is important for the rare-earth atoms. The spin-orbit interaction, together with the crystalline field, is the source of magnetic anisotropy of rare-earth atoms in these compounds. In this stage, the calculation including spin-orbit coupling may be important for a quantitative comparison.

In conclusion, we have studied the electronic structure of permanent magnetic materials RFe$_{11}$TiN$_x$ (R=Y, Nd, and Sm; x=0,1) using the LMTO-ASA band method. By comparing our full electron calculation with that for Y compounds, or using the frozen core approximation, the main conclusions can be summarized as (1) studies for Y compounds can give correct results of the magnetic moment of Fe atoms; (2) the 4f electrons of the rare-earth atoms do have hybridization with other valence electrons to some degree; and (3) a full electron calculation can give the correct relation of moments between rare-earth and iron atoms.

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