**Ab initio** Disordered Local Moment Approach for a Doped Rare-Earth Magnet

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Following the finite-temperature *ab initio* calculation framework based on the relativistic disordered local moments [1], we computationally demonstrate the possibility of doping-enhanced coercivity at high-temperatures, taking YCo\(_5\) as a working material in order to extract the 3\(d\)-electron part of the electronic structure of the rare-earth permanent magnets. Alkaline-earth dopants are shown to be the candidates to realize the proposed phenomenon.

**KEYWORDS:** rare-earth magnets, first principles, relativistic disordered local moment, magnetic anisotropy

1. **Introduction**

1.1 Motivation

Demands for an economically robust way to improve the merits of rare-earth permanent magnet materials at high temperatures has been recently sought [2]. One of the most important merits is the coercivity \(H_c\), which is the resistance of magnetization against the externally applied reverse-direction magnetic field. Coercivity seems to be realized by both of the extrinsic factors such as the microstructure and the intrinsic factors such as the strength of the magnetic anisotropy [2]. In the present work we focus on the latter which can be addressed within solid state physics, and give *ab initio* results for magnetization \(M\) and the uni-axial magnetic anisotropy energy (MAE) \(K_{u1}\) at finite temperatures. Our data can meet the demand for coercivity under the empirical relation that \(H_c\) is roughly proportional to the anisotropy field,

\[
H_A = \frac{2K_{u1}}{M}.
\]

The merit of the intrinsic properties of permanent magnets is characterized on a two-dimensional parameter space spanned by \(K_{u1}\) and \(M\) as schematically shown in Fig. 1.

To put more specifically the problem, we wish to find a way to enhance the high-temperature coercivity of today’s champion magnet Nd\(_2\)Fe\(_{14}\)B without resorting to Dy doping, which is thought to work mostly to enhance the ground-state anisotropy field [3]. Among the magnetically-relevant electrons in rare-earth permanent magnets which are

- 4\(f\)-electrons localized on the rare-earth atoms,
- 3\(d\)-bands from the transition metals, and
- 5\(d\)-bands from the rare-earth that couples the above two,

the high-temperature tail of the magnetic anisotropy is mostly carried by 3\(d\)-electrons [4]. We propose a way to enhance the high-temperature anisotropy field by engineering the 3\(d\)-electrons, which could...
Fig. 1. Schematic picture to show the target scope for the next-generation permanent magnet and the status of the working material in the present calculation. Even though the magnetic anisotropy can show a non-monotonic temperature dependence for some rare-earth magnets [3], the target scope is practically drawn with a set of representative numbers taken at the room temperature.

potentially lead to an alternative scheme to Dy-doping. We take the case of YCo$_5$ which represents one of the simplest 3$d$-electron physics in rare-earth permanent magnets and implement the 3$d$-band engineering by a hole doping [5].

1.2 The target material YCo$_5$

![Crystal structure of YCo$_5$ (a) with a bird’s eye view and (b) as projected onto the $ab$-plane. We have set the $z$-axis along the crystallographic $c$-axis.](image)

The permanent magnet material YCo$_5$ consists of the Co(2c) honeycomb lattice along the $ab$-plane, of which center the rare-earth (RE) (here Y) resides, Co(3g) kagomé lattice along the $ab$-plane, and Co(2c)-Co(3g) almost regular tetrahedra that are chained along the $c$-axis as shown in Fig. 2 (a) with the plot for the unit cell as projected onto the $ab$-plane in Fig. 2 (b).
1.3 Methods

We follow \textit{ab initio} relativistic disordered local moment approach (DLM) \cite{1} based on Korringa-Kohn-Rostoker (KKR) method and coherent-potential approximation (CPA) to address the MAE at finite temperatures. The basic idea is to express the free energy of a given material as

\[ F(\mathbf{n}) = F_{\text{iso}} + K_{u1} \sin^2 \theta \]

where \( F_{\text{iso}} \) is the isotropic part, \( K_{u1} > 0 \) is the MAE for uni-axial MCA and \( \theta \) is the angle between the direction of magnetization and the easy axis. For a uni-axial magnet, we fix the direction of magnetization to be \( \mathbf{n} = (1,0,1)/\sqrt{2} \) that is, \( \mathbf{n} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \) with \( \theta = \pi/4 \) and \( \phi = 0 \), and calculate the magnetic torque

\[ T_\theta \equiv -\frac{\partial F}{\partial \theta} = -2K_{u1} \sin \theta \cos \theta \]

with \( T_{\theta=\pi/4} \) to get

\[ K_{u1} = -T_{\theta=\pi/4}. \]

The full details of the free energy in DLM are described in Ref. \cite{1} and the sketch of them is given in Sec. II A in Ref. \cite{5}.

2. Doping-induced enhancement of the finite-temperature anisotropy field

2.1 The strategy

![Graphical representation](image)

\textbf{Fig. 3.} (a) Calculated filling dependence of MAE for YCo\textsubscript{5} near \( T = 0 \). The filling is measured with the electron number at the Fermi level (which is 54, including Y(4p)-band in the valance states) set to be zero. (b) The same thing is plotted as a function of the relative energy as measured in Kelvins from the position of the Fermi level.

Calculated magnetic anisotropy energy \( K_{u1} \) for the undoped YCo\textsubscript{5} near the ground state is shown in Fig. 3 (a) as a function of the number of valence electrons. The horizontal axis is plotted relatively to the valence electron number right on the Fermi level, which is \( N_e = 54 \). For the calculations of hole doping effects, we include Y(4p)-band in the valance states to add up 6 electrons to \( N_e = 48 \). The latter number is indeed the standard one found in the literature \cite{6} for the undoped case. We observe a peak structure which seems to originate in filling up an electronic state which carries the magnetic anisotropy. Now the idea is to focus on the particle-hole excitations that happens near the Fermi level \( \Delta N_e = 0 \) at finite temperatures. That would just lead to the temperature decay of \( K_{u1} \) on \( \Delta N_e = 0 \)
while if the filling is fixed to be $\Delta N_e \approx 0$, finite temperature effects could enhance $K_{u1}$ by filling up the electronic state that correspond to the peak in Fig. 3 (a).

In order to figure out the distance to the peak position as measured in terms of the temperature scale, the same data for $K_{u1}$ is shown in Fig. 3 (b) as a function of the manually-swept Fermi energy as measured from the one for the undoped case. The scale of the typical operating temperature range for permanent magnets, $200 \text{ [K]} \lesssim T \lesssim 500 \text{ [K]}$, is seen to correspond to the filling variation of a few of 0.1 electrons. Thus we set up computational sample materials to dope 0.1 or 0.2 holes in the unit cell of YCo5 by some element replacements and monitor the temperature dependence of their $K_{u1}$. Below we discuss two cases, $Y_{1-x}Ca_xCo_5$ and $YCo_{5-x}Cu_x$.

2.2 Replacing rare-earth with alkaline-earth

One of the standard ways to implement the hole doping has been to replace tri-valent rare-earth elements by di-valent alkaline-earth dopants. Here we replace Y by Ca in YCo5 and calculate the temperature dependence of the uni-axial MAE, $K_{u1}$. The results are shown in Fig. 4. Indeed some temperature enhancement is numerically observed in the high-temperature data at $T > 550 \text{ [K]}$ for the doping ratio $x = 0.1$ and 0.2 in $Y_{1-x}Ca_xCo_5$.

![Fig. 4. Calculated temperature dependence of MAE for Ca-doped YCo5.](image)

Remarks on $YCo_{5-x}Cu_x$ It is expected that Cu dopes electrons rather than holes when it replaces Co in YCo5. Indeed doping Cu shifts the calculated Fermi level upward and computational samples indeed have more electrons, but we have numerically observed that the peak position of MAE shifts upward on the $N_e$ axis even faster, thus an effective hole doping effects seem to be at work for the MAE of $YCo_{5-x}Cu_x$. However Cu dilutes the magnetically active 3$d$-electrons on Co and the bulk MAE gets just weaker and weaker with respect to Cu doping. Thus we have not been able to numerically demonstrate the temperature enhancement of MAE around such diminished peak.

3. Conclusions and Outlook

We have demonstrated the doping-enhanced coercivity at high temperatures [5] with the real-element dopant Ca onto Y. Alloying with other alkaline-earth dopants, Sr or Ba, to make $Y_{1-x}Sr_xCo_5$ and $Y_{1-x}Ba_xCo_5$, would also be the candidate materials to monitor the 3$d$-electron dominated magnetic anisotropy to demonstrate the enhancement of high-temperature coercivity. Holes can be doped either chemically as we have calculated or by a slight application of positive electric voltage, which could also be useful for improving the high-temperature coercivity of Nd2Fe14B.
In the present work, we have focused on a framework for a) $3d$-electron engineering. The next target material would be GdCo$_5$ where we can extract the $5d$-electron part and discuss b) $5d$-electron engineering as well from first principles. c) Engineering on $4f$-electron part is investigated on the basis of LDA+DMFT [7]. All of the above a)-c) is now being pursued to computationally implement the elements strategy for permanent magnets.

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