Site-preference and valency for rare-earth sites in (R-Ce)2Fe14B magnets

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Partitioning of Ga and Co atoms in a Fe 3 B/Nd 2 Fe 14 B nanocomposite magnet
Site-preference and valency for rare-earth sites in (R-Ce)$_2$Fe$_{14}$B magnets

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Rare-earth (R) permanent magnets of R$_2$Fe$_{14}$B have technological importance due to their high energy products, and they have two R-sites (Wyckoff 4f and 4g, with four-fold multiplicity) that affect chemistry and valence. Designing magnetic behavior and stability via alloying is technologically relevant to reduce critical (expensive) R-content while retaining key properties; cerium, an abundant (cheap) R-element, offers this potential. We calculate magnetic properties and Ce site preference in (R$_{1-x}$Ce$_x$)$_2$Fe$_{14}$B [$R = La, Nd$] using density functional theory (DFT) methods—including a DFT + U scheme to treat localized 4f-electrons. Fe moments compare well with neutron data—almost unaffected by Hubbard U, and weakly affected by spin-orbit coupling. La$_2$Fe$_{14}$B, Ce alloys for $0 \leq x \leq 1$ and prefers smaller (4f) sites, as observed, a trend we find unaffected by valence. Whereas, in Nd$_2$Fe$_{14}$B, Ce is predicted to have limited alloying ($x \leq 0.3$) with a preference for larger (4g) sites, resulting in weak partial ordering and segregation. The Curie temperatures versus $x$ for (Nd,Ce) were predicted for a typical sample processing and verified experimentally. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4789527]

With the discovery of R$_2$Fe$_{14}$B compounds,¹ and their high energy products ($BH$)$_{max}$, permanent magnets achieved significant technological impact—from phones, traction motors, to wind-energy applications—products are smaller, lighter, and more energy efficient. ($BH$)$_{max}$ is the maximum product for magnetic induction B versus reversed applied field H. Over the years, permanent magnet materials of increasing ($BH$)$_{max}$ have been found, including steels, AlNiCo, hard ferrites, and SmCo$_5$, but R$_2$Fe$_{14}$B compounds remain the most potent, with ($BH$)$_{max}$ as large as 64 MGOe. The most studied R$_2$Fe$_{14}$B prototype is Nd$_2$Fe$_{14}$B, with a crystal structure established by neutron powder-diffraction¹ and single-crystal x-ray analysis.⁶ From a commercial standpoint, cheaper isostructural compounds with equal or better magnetic properties are always desired, so various isostructural R$_2$Fe$_{14}$B compounds were investigated and their properties analyzed.³ Due to the increasing demand of permanent magnets in traction motors, and given continued supply restrictions on rare-earths, it is a priority to develop materials that do not rely on scarce R-elements—Nd, Pr, Dy, etc. La and Ce are the most abundant rare-earths, hence our choice for the present study.

To understand the effects of site-preference and chemical disorder, one must appreciate the R$_2$Fe$_{14}$B tetragonal structure (space group P4$_2$/mmn). Each unit cell has four formula units or 68 atoms. Denoting the 68 atoms by atom type, site multiplicity, and Wyckoff label, there are two crystallographically inequivalent R-sites [R(4f) and R(4g)], six inequivalent Fe sites [(Fe16k1), (Fe16k2), (Fe8j1), (Fe8j2), Fe(4e), and Fe(4c)], and one kind of B site [B(4g)]. The intricate structure and planar projections were shown by Herbst.³ For insight, we show also a repeating motif (besides the hexagonal Fe structure) in Fig. 1(a), a trigonal prism formed by two kinds of Fe, with B in the center bonding to three R through three faces. For a pseudoternary (R$_{1-x}$Ce$_x$)$_2$Fe$_{14}$B alloy, (R,Ce) can take various configurations (on two R-sublattices) at different $x$, including solid solution, partially ordered or perfectly ordered phase, see Fig. 1(b).

In Ce$_2$Fe$_{14}$B, cerium has an assessed⁴ valence of 3.44—an admixture of trivalent (3⁺) 4f$^1$ and tetravalent (4⁺) 4f$^0$ electronic states—forming a mixed-valence $x$-state, and lacking a stable localized 4f-moment.⁴ The Ce mixed valence significantly impairs magnetic behavior. Hence, developing a reliable Ce-based magnet with improved magnetic properties requires engineering the R-sites to ensure that all Ce adopt either a trivalent (3⁺) $\gamma$-state, or a tetravalent (4⁺)—all or nothing could offer superior magnetic properties. Notably, the Ce valence depends on its steric volume,⁴,⁵ i.e., local environment. So, one way of manipulating valence is to vary the unit cell volume by forming pseudoternary (R$_{1-x}$Ce$_x$)$_2$Fe$_{14}$B compounds.

We investigate the stability and site preference of Ce in (R$_{1-x}$Ce$_x$)$_2$Fe$_{14}$B [$R = La, Nd$]. In (La,Ce)$_2$Fe$_{14}$B, a partial disordered phase is found to be stable with the smaller R(4f) sites (Fig. 1) preferred for Ce, as assessed experimentally.⁶ For (Nd,Ce)$_2$Fe$_{14}$B, we predict that Ce prefers the larger R(4g) sites, explained by atomic size effects. While this requires experimental confirmation, it is supported by recent dichroic resonant x-ray diffraction experiments⁷ on Nd$_2$Fe$_{14}$B, suggesting that the superior magnetocrystalline anisotropy favoring c-axis arises from Nd(4g) sites, while Nd(4f) sites undermine this by favoring moments oriented in the basal plane.

We use two density functional theory (DFT) methods to address alloying, spin-orbit, and Hubbard U effects—based on local spin-density approximation (LSDA) or generalized gradient approximation (GGA) by Perdew-Burke-Ernzerhof (PBE). We apply Vienna ab initio simulation package⁸ (VASP) with a pseudo-potential and projected-augmented-wave (PAW) basis⁹—see supplementary material for computational details.¹⁰ To address localized f-electrons, we use
PBE + U\(^{10}\) with U introduced in a screened Hartree-Fock manner as an on-site LSDA replacement. As spin-orbit coupling (\(L \cdot S\)) to the lattice of the hybridized R(4f)-Fe(3d) level is stronger than that of Fe(3d), sensitivity of magnetism to spin-orbit was checked.

VASP is computationally demanding for defected cells of complex alloys and cannot address chemical disorder directly. Ordered cell approximates do not always describe chemical disorder well, e.g., as for quantum criticality in NbFe\(_2^{11}\). Thus, we use an all-electron Korringa-Kohn-Rostoker combined with the coherent potential approximation (KKR-CPA)\(^{12}\) to address the alloying, stability, and site preference in homogeneously disordered, and partially and perfectly ordered cases. Details of the KKR-CPA calculation, especially \(T_c\) estimation, can be found elsewhere.\(^{13,14}\) Formation energies versus \(x\) were verified in selected ordered cases with VASP, agreeing within 20%. For Nd\(_2\)Fe\(_{14}\)B, relaxations within LSDA gave lattice constants within 2% of experiment.\(^3\) Yet, we used the observed parameters in all our calculations to provide the correct electron/volume for more proper comparison with experiment.

Magnetic moments on inequivalent Fe and R-sites (R = Nd, Ce\(^{3+}\), Ce\(^{4+}\)) in R\(_2\)Fe\(_{14}\)B show little dependence on U (see supplementary Fig. S1). Due to hybridization of R(4f)-Fe(3d) levels, spin-orbit coupling can be important. So, we investigated the effects of Ce valence on Fe moments. In Fig. 2, we show moments with(out) spin-orbit coupling for Nd\(_2\)Fe\(_{14}\)B (top) with good agreement to experimental data,\(^{15}\) and for Ce\(_2\)Fe\(_{14}\)B with Ce\(^{4+}\) (middle) and Ce\(^{3+}\) (bottom). Spin-orbit is more significant in Nd\(_2\)Fe\(_{14}\)B, as observed, because Nd has \(L = 6, S = 3/2\) compared to Ce\(^{3+}\) \(L = 3, S = 1/2\). But, in Ce\(_2\)Fe\(_{14}\)B, Ce shows mixed-valence behavior. Moments on Fe-site are unchanged for Ce\(^{4+}\), as expected from having no 4f-3d hybridization. For Ce\(^{3+}\), a more accurate \(L \cdot S\) calculation shows a reduction in Fe moments and \(T_c\), as observed. Calculated orbital moments on Fe-sites are given in Table I. The Fe-orbital moments yield a better comparison to experiment\(^{15}\) when added to the spin moments, see Fig. 2.

With moments validated in parent compounds, we next study the stability of (R\(_{1-x}\)Ce\(_x\))\(_2\)Fe\(_{14}\)B as Ce substitutes on R

<table>
<thead>
<tr>
<th>System</th>
<th>Fe((k_1))</th>
<th>Fe((k_2))</th>
<th>Fe((j_1))</th>
<th>Fe((j_2))</th>
<th>Fe((e))</th>
<th>Fe((c))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd(<em>2)Fe(</em>{14})B</td>
<td>0.045</td>
<td>0.041</td>
<td>0.041</td>
<td>0.044</td>
<td>0.043</td>
<td>0.047</td>
</tr>
<tr>
<td>Ce(^{3+})Fe(_{14})B</td>
<td>0.047</td>
<td>0.039</td>
<td>0.038</td>
<td>0.042</td>
<td>0.047</td>
<td>0.043</td>
</tr>
</tbody>
</table>
sites. Figure 3 shows the formation energies versus $x$ for $(R_{1-x}\text{Ce}_x)_{2}Fe_{14}B$ [$R =$ La, Nd] for various configurations indicated in Fig. 1(b). Our KKR-CPA code$^{16}$ was used to calculate all configurations in a parent cell. First, we validate our calculations via La-Ce because some phase stability and Ce site preference have been assessed experimentally. We then contrast with Nd-Ce, which have limited experimental data. Notably, site preference is different in the two compounds, which is a key to controlling valence and stability.

La-Ce alloying supports a solid-solution (homogeneous R-site disorder) over all $x$, see Fig. 3, as observed.$^{6,17}$ Surprisingly, we find that a partially ordered phase (squares) is more stable at 25% and 75% Ce, where Ce occupies the smaller R(4$f$) site over all $x$. At 50%, such a configuration forms a perfectly ordered compound, i.e., all Ce at R(4$f$) and La at R(4$g$). Thus, Ce has a calculated site preference in $(La_{1-x}Ce_x)_{2}Fe_{14}B$ for the R(4$f$) sublattice. Indeed, this was reported from x-ray absorption near-edge spectroscopy (XANES) measurements.$^6$

In contrast, a homogeneously disordered phase is unstable at 0 K in $(Nd_{1-x}Ce_x)_{2}Fe_{14}B$. The lack of a solid solution (for $x > 25\%$) is known from experiment$^{18}$ but the extent of homogeneity was not determined, and high-T annealing leads to homogenization. So, the solid solution phase may indeed show partial disorder, rather than being homogeneous. In fact, our ongoing experiment$^{19}$ found a two-phase region in the spectrum emission mask image above $x = 25\%$, supporting the lack of homogeneous disorder. By Maxwell construction, our results predict a weakly stable partially ordered phase (red square) at 25% Ce, but none at higher %Ce, where segregation is found. We hope to confirm this by analyzing the inhomogeneity. The instability at larger %Ce is due to a 15%-20% difference in Nd$_2$Fe$_{14}B$ and Ce$_2$Fe$_{14}B$ volumes and the difference in Nd and Ce valences, which, from a thermodynamic model, suggest a maximum solubility of 40% Ce. No calorimetric data yet exist to verify our predictions.

In Nd-Ce, Ce prefers R(4$g$) sites, but R(4$f$) sites in La-Ce, a trend explained from atomic size. In 2-14-1 structure, from the coordination shell around R-sites, R(4$f$) sites are smaller in volume than R(4$g$); as such, a bigger (smaller) atom prefers the larger (smaller) site, and a Ce$^{3+}$ ion is smaller than La$^{3+}$, but larger than Nd$^{3+}$.

Alloying Ce on R-sites barely affects the Fe moments, $\mu$. Magnetizations on R-sites, however, change dramatically from alloying and valence effects. Figure 4 shows $\mu$ versus $x$ on R(4$f$), R(4$g$), and Ce(4$g$) sites for $(La_{1-x}Ce_x)_{2}Fe_{14}B$ (top) and $(Nd_{1-x}Ce_x)_{2}Fe_{14}B$ (bottom) in their lowest-energy configurations. Results for both Ce$^{4+}$ and Ce$^{3+}$ are provided. La accumulates small induced moment (antiferromagnetically (AFM) aligned to Fe) similar to Ce$^{4+}$ moments in both alloys remain almost the same as in Ce$_2$Fe$_{14}B$. La moments also remain similar to the parent compound. With Ce$^{4+}$, Nd moment also remains unchanged.
over all %Ce. For Ce$^{3+}$, La and Ce behave mostly same as Ce$^{4+}$, except with a larger AFM moment due to the extra contribution from 4f electrons.

Notably, Nd magnetization changes orientation at $x = 0.5$, with a larger AFM moment ($-3.5\mu_B$) on 4f sites compared to 4g sites ($-1.5\mu_B$). Such a transition of the Nd magnetic state causes an overall reduction of the net magnetization of the cell, and is the reason for instability at higher %Ce. It is thus clear that magnetic alignment can be affected if both the alloying species possess a 4f-electron, which causes a different nature of hybridization, as in case of $(\text{Nd},\text{Ce})_{2}\text{Fe}_{14}B$.

To further validate our predictions, we measured Curie temperatures, $T_c$, versus $x$, for polycrystalline buttons of $(\text{Nd},\text{Ce})_{2}\text{Fe}_{14}B$ prepared by arc melting in argon—see supplementary material for more details. The magnetization, $M(T)$, versus $T$ was measured from 300 to 800 K in a field of 1000 Oe using a physical property measurements system from Quantum Design, Inc. The derivative of $M(T)$ provided $T_c$s. Figure 5 compares our measured and calculated $T_c$. We assume a mean-field theory (MFT) relation between $T_c$ and the KKR-CPA energy differences between ferromagnetic (FM) and paramagnetic (approximated by disordered local moments) phases, which gives a 5% error for $T_c$ in non-RE alloys. A high-T anneal was used in experiment, so a Nd-Ce solid solution was used in the KKR-CPA calculation. MFT, ignoring local R moments, overestimates $T_c$ (a constant shift of 175 K) but reproduces the observed trend for $T_c$ vs. $x$, see Fig. 5. $T_c$ is controlled by 3d-3d and R-Fe exchanges. With Ce substitution, the Nd-Fe exchange is weakened from a decrease in the de Gennes factor—see further explanation in supplementary material. A larger effect, however, is a decrease in 3d-3d exchange from alloying and associated volume decrease, giving a linear drop in $T_c$ with %Ce, as observed.

In summary, we investigated magnetism and site preferences from Ce alloying, and the effects of spin-orbit and localized 4f-electrons in R$_2$Fe$_{14}$B (R = La, Nd) permanent magnets. Spin-orbit correctly captures the hybridization effects, improving agreement of calculated moments with experiment. The Ce site preference was validated in La-Ce and predicted in Nd-Ce compounds. To help engineer the Ce valence and induce Ce$^{3+}$, the stability and favorable alloy configurations in (R-Ce)$_2$Fe$_{14}$B were examined. Alloyn helps control cell volume and Ce valence, due to the steric volume dependence of Ce-valence and alloying site preference. In La-Ce compounds, a reduction of Ce content can change Ce from a mixed-valence $\alpha$-state to a trivalent $\gamma$-state with a localized 4f moment. Alloyn homogeneously in Nd-Ce compounds shows a site preference for Ce opposite to that in La-Ce; but, above 25%Ce the Nd magnetization changes from FM to AFM, leading to a structural instability (segregation) at low temperatures. The calculated and measured $T_c$ provides a validation of our predictions. Using these results as a guide, we are now investigating doping Sc, Y, or La in (Nd-Ce)$_2$Fe$_{14}$B, quantifying the Ce mixed-valence energetics, as well as Co doping for Fe to alter Ce site-preference and valence to enhance magnetic performance at lower cost.

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19M. Khan, private communication (2012).
20See supplementary material at http://dx.doi.org/10.1063/1.4789527 for “U” dependence of magnetic moments and further computational and experimental details.