

Calculating Curie temperatures for rare-earth permanent magnets: *Ab initio* inspection of localized magnetic moments in *d*-electron ferromagnetism

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We present a data set of calculated Curie temperatures for the main-phase compounds of rare-earth permanent magnets. We employ *ab initio* electronic structure calculations for itinerant ferromagnetism and an effective spin model for finite-temperature magnetism. Curie temperatures are derived on the basis of a classical Heisenberg model mapped via Liechtenstein's formula for atomic pairwise exchange couplings. Relative trends with respect to the species of rare-earth elements in calculated Curie temperatures for $R_2\text{Fe}_{14}\text{B}$ are in agreement with experimental trends. A quantitative comparison between calculation and experimental data found in the literature points to an effective range of exchange couplings imposing a limit on the validity range of the effective spin model.

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I. INTRODUCTION

The global concern for sustainable energy supplies in terms of environmental friendliness, and the preservation of natural resources, puts rare-earth permanent magnets (REPMs) as one of the most critically important materials for the future of human society. Today's commercial REPMs are made of Fe and rare-earth elements such as Nd, and issues associated with the usage of REPM at high temperatures have posed a renewed interest in the magnetism of Fe-based materials at finite temperatures. In today's commercial champion magnet the main-phase compound $\text{Nd}_2\text{Fe}_{14}\text{B}$ [1–3] comes with a relatively low Curie temperature of 585 K, almost half of the Curie temperature of elemental Fe at 1043 K. Considering the high-temperature range of the practical usage of traction motors of cars up to 450 K, it has been in high demand to find a way to supplement the high-temperature performance of Nd-Fe-B magnets or to design a new champion magnet with desirably higher Curie temperatures and good structural stability.

The question posed for solid state physics may boil down to finding an optimal material in a space spanned by (a) magnetization, (b) magnetic anisotropy, and (c) Curie temperature, all of which are backed up by (d) structural stability [4]. In the present paper we focus on the Curie temperature and magnetization which come from the leading-order energy scales in the intrinsic electronic structure of those $4f$ - $3d$ intermetallic compounds. The Curie temperature comes from the dominating $3d$ - $3d$ direct exchange couplings in the order

of 10 meV for each exchange path, which is multiplied by the coordination number in a lattice that is typically from 10 to up to around 20 in the immediate neighborhood of the magnetic atom [5]. Even a tiny amount of coupling in the long-range exchange path could contribute a lot considering the huge coordination number [6]. However, consideration of a too long-range exchange path involves a problem in resolving the localized magnetic moment contribution and the obvious itinerant contribution to the intrinsic magnetism. It is an important problem to understand how well we can make an *ab initio* prediction for those important properties (a)–(d) both for a fundamental theory of metallic magnetism and for practical demands in the past and future decades. The leading-order answer to the materials family including the champion magnet compound is presented in Fig. 1.

Clarification of the validity range of a spin model for itinerant magnetism would possibly lead to several possibilities for an optimal compound for permanent magnet utility in the middle of a subtle interplay between the localized and delocalized nature in the *d*-electron state. Here, a possible lesson may be found in the case of an exceptionally high Curie temperature for a Ce-based ferromagnet CeRh_3B_2 at 120 K [7,8] that is even higher than that of the Gd counterpart at 90 K. This problem has been known for almost as long as for $\text{Nd}_2\text{Fe}_{14}\text{B}$ (since the early 1980s), and the particular dual nature showing both localization and delocalization as probed by x-ray absorption spectroscopy [9] in a $4f$ -electron state of Ce has been discussed. Electronic states on the crossover between localized and delocalized electronic states are most fertile both in terms of fundamental solid state physics and practical functionalities, and we inspect the problem for *d*-electron ferromagnetism with some additional resolution of the particular exceptional contribution from Ce in $\text{Ce}_2\text{Fe}_{14}\text{B}$.

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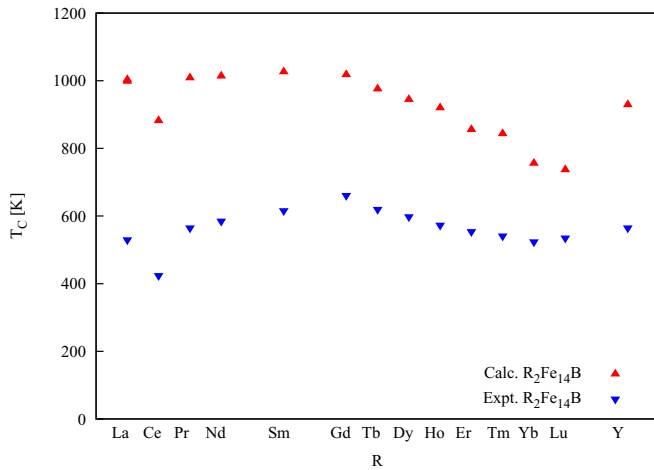


FIG. 1. Calculated Curie temperature T_C for the champion magnet compound $\text{Nd}_2\text{Fe}_{14}\text{B}$ and isostructural materials $R_2\text{Fe}_{14}\text{B}$ (R = rare earth) compared with experimental data. The input lattice information is taken from past experimental data [3].

The present paper is organized as follows. In the next section, our computational methods are described. The main results are shown in Sec. III. Discussions on the difference between the Fe-rich limit and Co-rich limit and lattice structure variants are given in Sec. IV. The final section is devoted to conclusions and outlook.

II. METHODS

For the champion magnet compound $\text{Nd}_2\text{Fe}_{14}\text{B}$ and related ferromagnets, we address the ferromagnetism and the expected Curie temperature on top of it via *ab initio* electronic structure calculations on the basis of the Korringa-Kohn-Rostoker Green's function method as implemented in AKAI-KKR [10]. Our calculations are based on the local density approximation (LDA), taking the exchange correlation function following Vosko, Wilk, and Nusair [11]. Presented below are data on the basis of the atomic-sphere approximation (ASA). The muffin-tin approximation basically yields the same trends as has been given by ASA for the present purpose to address magnetization and exchange couplings. No further parameters are involved in our first-principles calculations: We will see that plain LDA works for $4f$ - $3d$ intermetallics which may be compared to the description of the ferromagnetic ground state of bcc Fe on the basis of LDA.

The electronic states of rare-earth elements are treated within the open-core approximation in order to inspect the trends among the exchange couplings between $3d$ electrons that dominate the Curie temperature in the leading order [5,12]. A trivalent state is assumed for rare-earth elements except for Ce. Ce is set to be in a tetravalent state in Ce-Fe/Co intermetallics, due to the exchange splitting of conduction bands spanning the energy width of a few eV while the $4f$ -electron level in Ce compounds, if localized, sits at a position as shallow as only up to 2 eV below the Fermi level [13]. Thus it is not very likely for the $4f$ electron in Ce to be kept in the localized level when it is put in the exchange-split conduction band made of $3d$ electrons coming from Fe or Co.

Recently, the construction of spin models for the finite-temperature magnetism of $\text{Nd}_2\text{Fe}_{14}\text{B}$ has been attempted by several groups [6,14–20]. We employ the most simplified form of them to give an overview of the trend in the calculated Curie temperatures. Nonrelativistic calculations are employed which should be sufficiently precise to extract the trends in magnetization and exchange couplings. For a converged ferromagnetic state of each target material, interatomic exchange couplings are determined following Liechtenstein *et al.* [21]. An effective spin Hamiltonian which goes as $\mathcal{H} = -\sum_{\langle i,j \rangle} 2J_{i,j} S_i S_j \mathbf{e}_i \cdot \mathbf{e}_j$ is used to survey the trends in the Curie temperature on the basis of the mean-field approximation (MFA). Here, the site index i specifies an atom on which the localized magnetic moment of the magnitude S_i and the direction as pointed by the unit vector \mathbf{e}_i is assumed. Summation over the exchange path between sites i and j runs only once on each path $\langle i, j \rangle$. The range of the exchange couplings is incorporated without any cutoff and all of the exchange couplings in the metallic ferromagnetism are directly plugged into the mean-field approximation on the basis of the KKR Green's function method. Only $3d$ electrons from Fe or Co and $5d$ electrons from rare-earth elements are considered in the spin Hamiltonian, on the basis of the open-core approximation for rare-earth elements. The systematic error originating in MFA can be eliminated by a numerically exact solution of the spin Hamiltonian via Monte Carlo methods [5,6,22] while a more fundamental error between theory and experiment can come in from the discrepancy between itinerant ferromagnetism and the localized spin model. This is what we wish to address through the inspection of the trends between the MFA data on the basis of the *ab initio* electronic structure and the experimental data.

III. RESULTS

The calculated magnetization for $R_2\text{Fe}_{14}\text{B}$ is shown in Fig. 2. Taken together with the results shown in Fig. 1, the experimental trends of the intrinsic ferromagnetism in the 2:14:1 material family with respect to the species of rare-earth (RE) elements are reasonably well reproduced on the basis of our electronic structure calculations involving only d electrons. Intrinsic ferromagnetism concerning the exchange couplings has been well described up to the leading order, on the basis of the precision for the total magnetization where the $4f$ -electron contribution can be restored on top of the results from open-core calculations. Results for Co analogs are shown in Fig. 3. Overall parallel trends between theory and experiments again hold but with an even better quantitative precision.

The decreasing trend in the Curie temperature of $R_2\text{Fe}_{14}\text{B}$, with R being the heavy rare-earth elements, can be attributed to lanthanide contraction, which seems to trigger the lattice contraction as we overlap another calculated Curie temperature with the lattice fixed to be that of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and the dependence on the chemical composition R is monitored. The results for this line of reasoning are presented in Fig. 4. The particular drop of the Curie temperature for $\text{Ce}_2\text{Fe}_{14}\text{B}$ in the overall trend in $R_2\text{Fe}_{14}\text{B}$ can be attributed to the exceptional tetravalent state and the corresponding lattice shrinkage. As seen in Fig. 4, fictitiously restoring the trivalent

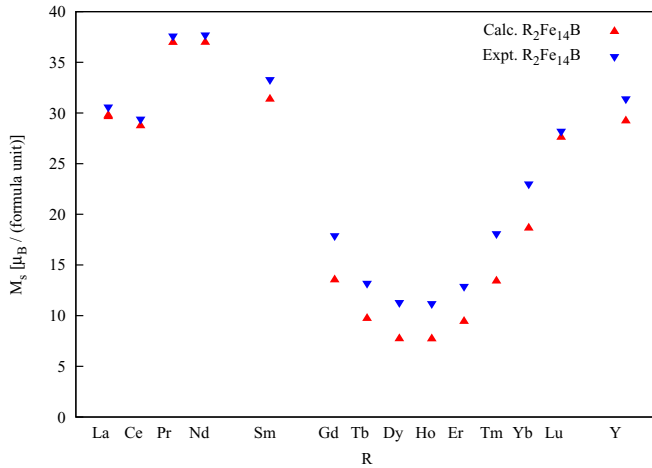


FIG. 2. Calculated magnetization for $R_2\text{Fe}_{14}\text{B}$ (R = rare earth) compared with experimental data [3]. In our results based on an open-core treatment for rare earth, the contribution from $4f$ electrons has been manually added by $\pm g_J \sqrt{J(J+1)}$, where the signs $+/-$ are used for light/heavy rare earths, respectively, except for $R = \text{La}$, Ce , Lu , and Y where no $4f$ electron contribution was assumed. Here, J is the total magnetic moment for each rare earth and g_J is the Landé g -factor.

state for Ce brings up the Curie temperature and putting $\text{Ce}_2^{3+}\text{Fe}_{14}\text{B}$ on the same fixed lattice of $\text{Nd}_2\text{Fe}_{14}\text{B}$ brings about the smooth trend in the calculated Curie temperatures, in strong contrast to the parallel trends of the calculated Curie temperatures and experimental ones in Fig. 1. Inspecting the difference in the density of states (DOS) for $R_2\text{Fe}_{14}\text{B}$ on the fixed lattice and that on the experimental lattice with the lanthanide contraction, say, for $R = \text{Yb}^{3+}$ as shown in Fig. 5, we see that the lanthanide contraction has made the d -electron magnetism change into weak ferromagnetism in contrast to the strong ferromagnetism found for $\text{Nd}_2\text{Fe}_{14}\text{B}$ [23].

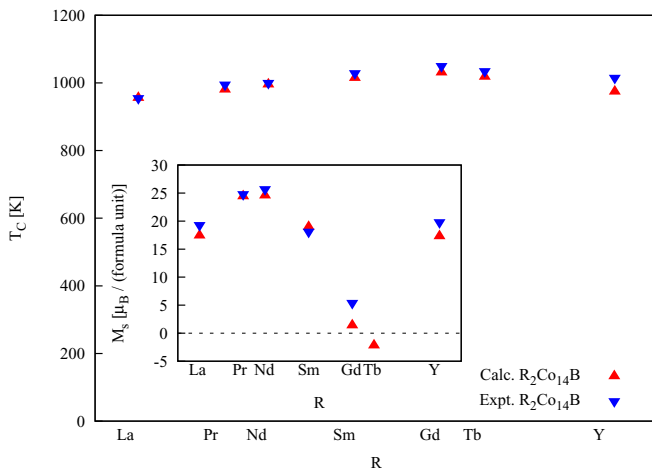


FIG. 3. Calculated Curie temperature for $R_2\text{Co}_{14}\text{B}$ ($R = \text{La}$, Pr , Nd , Sm , Gd , Tb , and Y). In the inset, magnetization of $R_2\text{Co}_{14}\text{B}$ calculated in the same way as is done in Fig. 2 is shown. For the input to our calculations, experimental lattice constants are taken from Ref. [3]. Experimental Curie temperatures and magnetization are also found in Ref. [3].

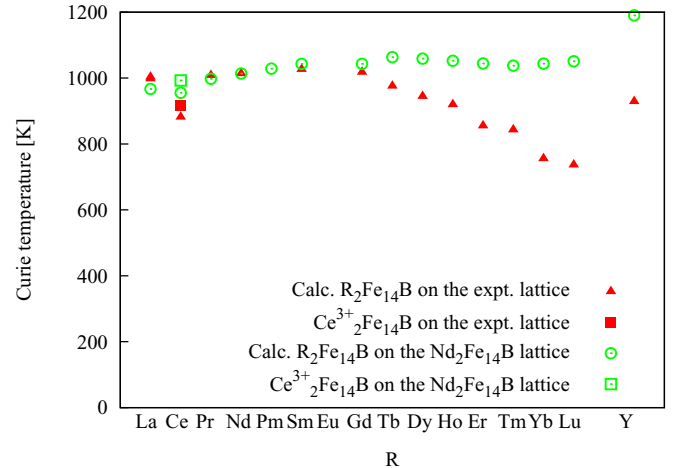


FIG. 4. Comparison of calculated Curie temperatures for $R_2\text{Fe}_{14}\text{B}$ on the fixed lattice of $\text{Nd}_2\text{Fe}_{14}\text{B}$ compared to the calculated data with the experimental lattice constants. For a further comparison, results with Ce^{3+} have been included. See the text for details.

IV. DISCUSSIONS

A. Inspection on the range of exchange interaction

We have seen that the effective Heisenberg model can describe the trends of magnetization and Curie temperature for $R_2T_{14}\text{B}$ with respect to R while the quantitative levels achieved for $T = \text{Fe}$ and $T = \text{Co}$ look quite different. To see how a spin model can be acceptable for the itinerant ferromagnetism, we come back to the reference elemental case studies with bcc Fe ($a = 5.417$ a.u.) and hcp Co ($a = 4.7377$ a.u. and $c/a = 1.623$). The calculated Curie temperature is 1200 K for bcc Fe and 1411 K for hcp Co, in reasonable agreement with the experimental data of 1043 K for bcc Fe and 1394 K for hcp Co on the basis of MFA. The exchange couplings in the spin Hamiltonian as calculated following Liechtenstein *et al.*'s approach [21] are shown in

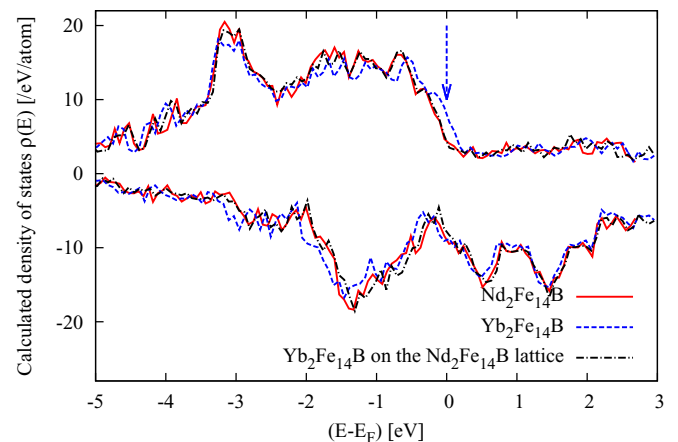


FIG. 5. Comparison of calculated density of states for $\text{Nd}_2\text{Fe}_{14}\text{B}$, $\text{Yb}_2\text{Fe}_{14}\text{B}$, with the experimental lattice constants, and a fictitious $\text{Yb}_2\text{Fe}_{14}\text{B}$ on $\text{Nd}_2\text{Fe}_{14}\text{B}$. The arrow in the figure points to the majority-spin density of states for the experimental lattice $\text{Yb}_2\text{Fe}_{14}\text{B}$, indicating the weak ferromagnetism.

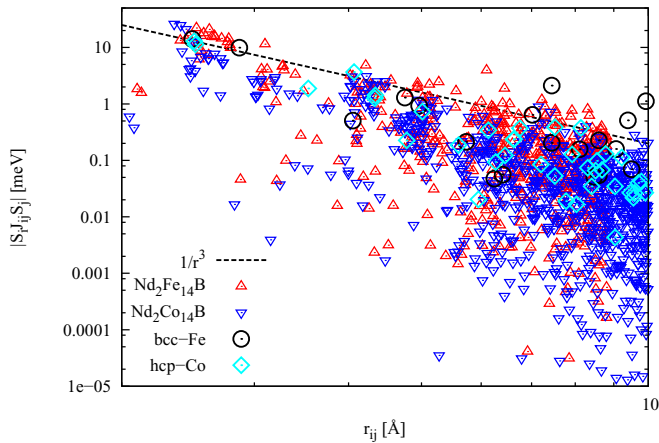


FIG. 6. Calculated exchange couplings for $\text{Nd}_2\text{T}_{14}\text{B}$ ($T = \text{Fe}$ and Co) are shown with the absolute values plotted as a function of the interatomic distances. The analogous data for bcc Fe and hcp Co are overlapped as a reference.

Fig. 6 together with the corresponding data for $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_2\text{Co}_{14}\text{B}$. The range of Fe-Fe exchange couplings is longer than Co-Co exchange couplings. Long-range couplings reflect the inherently itinerant electronic states [24]. The trend from weak ferromagnetism to strong ferromagnetism goes as bcc Fe, $\text{Nd}_2\text{Fe}_{14}\text{B}$, $\text{Nd}_2\text{Co}_{14}\text{B}$, and hcp Co, as can be seen in the calculated DOS shown in Fig. 7. Long-range exchange couplings come from the metallic nature in the electronic state. The overall trend is that the less metallic, the better a description has been achieved on the basis of the spin model. The description of bcc Fe could have been worse if the minority-spin band had more DOS around the Fermi level. An apparent reasonable description of bcc Fe on the basis of the simplified spin model might depend on the particular density of states where the diminishing DOS in the minority-spin band renders the system less metallic. This may compensate for the weak ferromagnetic nature with significant DOS in the majority-spin band, out of which the yielded ferromagnetism

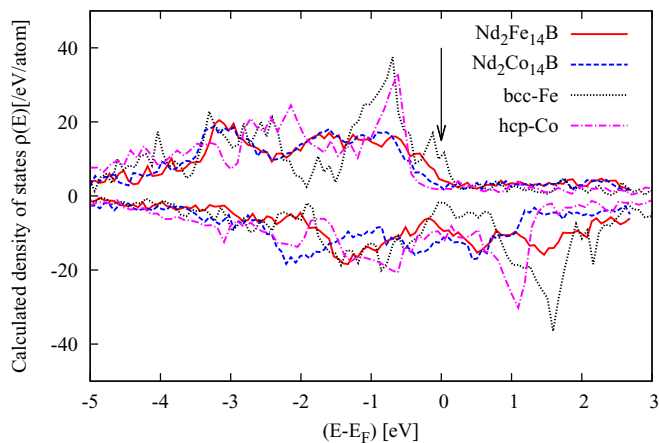


FIG. 7. Calculated density of states for $\text{Nd}_2\text{T}_{14}\text{B}$ ($T = \text{Fe}$ and Co) overlapped with bcc Fe and hcp Co. The arrow on the Fermi level points to the majority-spin states which show the weak ferromagnetism.

may not have been very suited for the description based on localized spins.

Strictly speaking, a spin-only model for itinerant magnetism is invalid by construction for quantitative studies while discussions focusing on the relative trends in a restricted range of chemical composition and lattice structure may well be justified [5,6] up to leading order. In addition, the anomalous temperature dependence of the lattice constants [25] observed in $\text{R}_2\text{Fe}_{14}\text{B}$ has been completely dropped from our present description of the Curie temperature. A proper incorporation of finite-temperature lattice dynamics should improve the calculated Curie temperature that is dominated by itinerant d -electron magnetism. Incorporation of the lattice effect in the description of finite-temperature magnetism on elemental Fe and Co has been done recently and the relevance of lattice effects especially for bcc Fe has been shown [26]. Common physics may well be at work in $\text{Nd}_2\text{Fe}_{14}\text{B}$.

B. Crystal structure trends

For $\text{Nd}_2\text{Fe}_{17}$ our calculated Curie temperature is $T_C = 670$ K. Compared with the experimental data of 326 K [27], the systematic overestimate is coming by a factor of 2.1, which is on par with what we got for $\text{Nd}_2\text{Fe}_{14}\text{B}$ where $T_C^{\text{calc.}}/T_C^{\text{expt.}} \simeq 1.7$. For $\text{Sm}_2\text{Co}_{17}$, our calculated Curie temperature is $T_C = 1173$ K, which compares well with the experimental number for 1200 K. The calculated Curie temperature is strongly influenced by the chemical composition: In the overall virtual parameter space spanned by the chemical composition and crystal structure, the composition of $3d$ metals plays a dominant role. In a “cross section” specified by a fixed chemical composition, the relative trends with respect to RE elements can be satisfactorily addressed.

V. CONCLUSIONS AND OUTLOOK

We have shown that the leading-order trends of the Curie temperature in the champion magnet compound family with respect to the species of rare-earth elements can be described from first principles focusing on the dominating d electrons. Care must be taken in addressing the trend of calculated Curie temperatures in the Fe-Co alloy on the basis of the effective spin model. The validity range of the spin-only description quantitatively differs between the all-Fe limit and all-Co limit. The strong ferromagnetism region in the Co-rich side characterized by a robust localized magnetic moment seems to be better suited for the spin model for a quantitative description. Within a subspace of fixed chemical composition, the relative trends in the intrinsic magnetism can be satisfactorily addressed on the basis of the effective spin model.

Having clarified the validity range of the spin model written in terms of localized degrees of freedom for the intrinsically delocalized ferromagnetism of $4f$ - $3d$ intermetallics, it is hoped that several possibilities for an optimal ferromagnetism for permanent magnet utility can be identified in the middle of the subtle interplay between the localized and delocalized nature in the d -electron state.

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