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Screening of rare-earth-lean intermetallic 1-11 and 1-11-X compounds of YNi_9In_2-type for hard-magnetic applications

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ABSTRACT

We report on theoretical investigations of ferromagnetic rare-earth-transition-metal phases with the structure of YNi_9In_2 and with additional atoms X at two interstitial positions. By a high-throughput-screening (HTS) approach based on density functional theory the intrinsic key properties of hard magnets, namely the magnetization M, energy product $(BH)_{max}$ and uniaxial magnetocrystalline anisotropy constant K_1 are estimated. The HTS identifies several promising phases $NdFe_{10}AX$ with A = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Si, P, and X = B, C, N. These phases partially outperform $Nd_2Fe_{14}B$ in terms of $(BH)_{max}$ and K_1 values, and they contain about 35% less rare-earth atoms.

The expanding market share of sustainable technologies like wind energy and electro-mobility will further increase the demand for high-performance hard magnets in the near future. Currently, $Nd_2Fe_{14}B$ doped with Dy is the benchmark and work-horse material in this field. But besides its moderate temperature performance it depends on the unforeseeable price development of the rare earth elements Nd and Dy. As a consequence, renewed world-wide research activities were started in recent years with the goal of finding new hard-magnetic compounds with comparable performance to $Nd_2Fe_{14}B$ but with significantly less or no contents of critical elements [1,2].

One focus of recent experimental and theoretical studies [3–11] is on intermetallic phases with the $ThMn_{12}$ crystal structure. These phases are interesting due to their favorable composition ratio of rare-earth (RE) and transition-metal (TM) elements, RE:TM = 1:12, and their uniaxial, namely tetragonal, crystal structure which is a necessary condition for uniaxial magnetocrystalline anisotropy. A similar beneficial ratio RE:TM = 1:13 can be obtained based on the $NaZn_{13}$-type crystal structure and its tetragonal $LaCo_9Si_4$ variant [12,13,16].

In this paper, our theoretical screening approach is extended to the YNi_9In_2 structure type [14] having an attractive ratio of RE:TM = 1:11. This structure is an ordered variant of $CeNi_5Mn_6$ in which the Ni and Mn atoms are randomly distributed over the TM sites [15]. Additionally, two variants of this 1-11 structure are considered. They are referred to as 1-11-X(2b) and 1-11-X(2d) in the following, and are obtained by inserting interstitial atoms on the unoccupied Wyckoff positions (2b) or (2d) of the YNi_9In_2 structure. It is shown that this kind of alloying with light interstitial elements X = B, C, or N can enhance the tetragonal distortion of the YNi_9In_2 structure. This geometric effect combined with chemical bonding effects of the interstitial X atoms [6-8,10,16] may increase the magnetocrystalline anisotropy significantly. Specifically, the results of our study indicate $NdFe_{11}X$ and $NdFe_{10}AX$ with substitutionals A = Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Al, Si or P and interstitials X = B, C, or N at (2b) sites as RE-lean intermetallic RE-TM compounds with potentially good intrinsic hard-magnetic properties.

The tetragonal YNi_9In_2 crystal structure belongs to space group No. 127 (P4/mbm). The lattice parameters of $NdNi_9In_2$ and the internal parameters determined experimentally by Bigun et al. [30] were taken as starting point for the construction of the unit cell of the 1-11 structure which contains 24 atoms in total (see Fig. 1, left). Since the analysis is focused on hard-magnetic applications with high magnetization a substantial amount of Fe contents is required for promising

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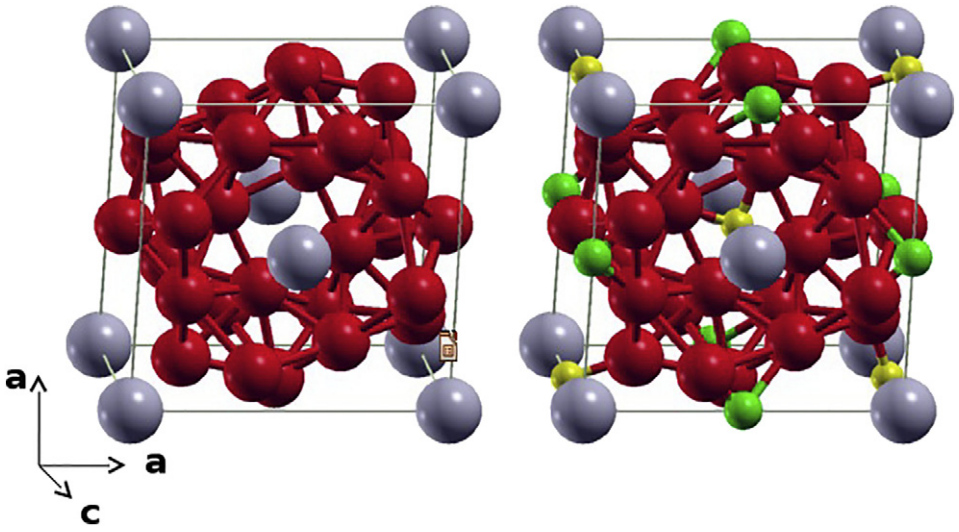

Fig. 1. Structure models of $NdFe_{11}$ (left) and the two realizations of the corresponding 1-11-X phases (right). Large grey and red spheres represent Nd and Fe atoms, respectively. Small yellow spheres represent interstitial atoms X = B, C, or N on Wyckoff position 2b in $NdFe_{11}X$(2b). Alternatively, small green spheres represent interstitial atoms on Wyckoff position 2d in $NdFe_{11}X$(2d). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

compounds. Therefore, in order to have a realistic structure model for the screening, the $NdNi_9In_2$-type structure with Fe atoms set on all TM sites was structurally optimized using density functional theory (DFT) with VASP [32,33] (see below for computational details). The lattice and internal parameters of this $NdFe_{11}$ structure were taken as input for the high-throughput screening (HTS) of the 1-11 compounds. Correspondingly, the two $NdFe_{11}N$ structure models, 1-11-X(2b) and 1-11-X(2d), each containing 26 atoms in the unit cell (see Fig. 1), were structurally optimized using VASP as well.

The structural parameters were kept fixed within the HTS procedure when substituting different RE, TM and interstitial elements (for discussion see our related work [10,16]). The structure parameters of $NdFe_{11}N$ were used as well for the HTS of phases containing B or C. Test calculations conducted a posteriori for the most promising candidate structures with optimized lattice and internal parameters of $NdFe_{11}B$ and $NdFe_{11}C$ indicated only small deviations (in the order of 1%) of the magnetic quantities relative to the results obtained with the structural parameters of $NdFe_{11}N$.

The structural optimization of the crystals was carried out using the projector augmented wave (PAW) method [31] as implemented in VASP [32,33]. The generalized gradient approximation (GGA) [34] was used for exchange-correlation, and PAW pseudopotentials with 14 and 5 valence electrons were used for Fe and N, respectively. For Nd we took the PAW potential which keeps the 4*f* electrons frozen in the core ("Nd_3")[35]. The number of 4*f* electrons in the core equals the number of valence electrons minus 3 which is the formal valence [35]. Elastic stresses and interatomic forces were relaxed using the BFGS algorithm. The calculations were carried out with a plane-wave cutoff energy of 680 eV, 3 × 3 × 5 Monkhorst-Pack [36] k-meshes and a Gaussian broadening of 0.05 eV.

The magnetic properties of the intermetallic compounds with the 1-11, 1-11-X(2b), and 1-11-X(2d) structures were examined using the HTS procedure set up by Drebov et al. [17] It allows a fully automated generation of new phases by combinatorial substitution of sets of equivalent atoms. Here, the Y sites of the YNi_9In_2 structure were occupied either by Ce, Nd, or Sm. The TM sites, originally occupied with Ni or In, were decorated with a variety of magnetic transition metal elements, namely Cr, Mn, Fe, Co, and Ni, and non-magnetic elements Al, Si, P, Ti, V, Cu and Zn. For the 1-11-X compounds we additionally inserted X = B, C, or N as interstitial elements. Overall, 1102 compounds containing Nd were assessed while for Ce and Sm we screened 453 compounds each [42].

Total energies as well as spin polarized electronic states and densities from which the physical properties are derived are calculated with the tight-binding (TB) linear-muffin-tin-orbital (LMTO) [18] atomic-sphere approximation (ASA) method of DFT [19,20]. The TB-LMTO-ASA calculations were performed using the local spin-density approximation (LSDA), the scalar-relativistic approximation of Koelling and Harmon [21] and the exchange-correlation functional of von Barth and Hedin [22] in the parametrization of Moruzzi et al. [23] Since the LSDA has a validity limited to weakly correlated systems, the strongly localized 4*f* electrons are treated by the "open core states" approach [24,25]. For the k-point sampling of the Brillouin-zone integrals the linear tetrahedron method and 6 × 6 × 10 Monkhorst-Pack meshes were used. In the ASA the supercell volume is subdivided into spheres, and as in our previous work [10,17] we rely here on the well-tested ratio for the atomic-sphere radii $r(\mathrm{RE})/r(\mathrm{TM})/r(\mathrm{IS}) = 1.35/1/0.7$ [26].

The DFT calculations yield the essential intrinsic crystal properties for the intermetallic phases, namely the magnetization *M*, the local magnetic moments, the anisotropy constant K_1, and the relative phase stability energy ΔE_f. The anisotropy field can be estimated from K_1 and M via the heuristic formula $H_a = 2K_1/(\mu_0 M)$. The TB-LMTO-ASA method determines the single crystal magnetization in good accuracy which allows an estimation of the energy product $(\mathrm{BH})_{\max}$ via the heuristic formula $(\mathrm{BH})^{EST}_{\max} = (0.9\mu_0 M)^2/(4\mu_0)$. This implies the common assumption that ideally about 10% of a processed bulk hard-magnetic microstructure consists of non-magnetic phases [6]. The calculation of the magnetocrystalline anisotropy (in terms of first order anisotropy constants K_1) is based on the single-ion-anisotropy model. A brief summary of this approach and its restrictions can be found in our related work [16]. For more details we refer the reader to the Refs. [10,20,27,28]. The formation energy ΔE_f of an intermetallic phase is calculated with respect to its elemental constituents and is an approximate indicator on whether a phase may be stable.

For the magnetocrystalline anisotropy there is in general a systematic quantitative discrepancy between theoretical predictions

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