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Magnetic, magnetocaloric and structural properties of manganese based monoborides doped with iron and cobalt – A candidate for thermomagnetic generators

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ABSTRACT

Refractory borides are good candidates for thermomagnetic energy conversion due to their high chemical stability and good magnetic properties. A systematic study focusing on the crystallographic, magnetic and magnetocaloric properties of cobalt and iron substituted MnB was conducted. The pure MnB sample shows an orthorhombic structure with a spontaneous magnetization (M_s) of 156 Am^2kg^{-1} and a sharp magnetic transition (T_C) of 567 K that yields a large magnetic entropy change of 7.5 J $kg^{-1}K^{-1}$ in a 2T field change at this temperature. Both the substitution of Co and Fe elements for Mn were found to effectively modify T_C accompanied by a lower magnetization (M_s) leading to a reduced magnetocaloric effect (MCE). The differences in magnetic properties with substitution are described by calculation of the density of states and interatomic distances. It is found that in contrast to the Co atoms the Fe atoms develop large and stable moments similar to the Mn atoms which is consistent with the experimental findings. The sharp and significant change of M_s(T), the very stable nature of these refractory borides and abundant availability makes some of these compositions suitable for thermomagnetic power generation applications.

1. Introduction

Magnetic refrigeration is currently a thriving research topic as it offers considerably higher energy efficiency compared to vapor compression refrigeration [1–4]. However, in a reverse process a magnetocaloric material can also be used to directly convert heat to electricity [5,6]. Brillouin and Iskenkenderian firstly estimated the efficiency of such a thermomagnetic generator to be as high as 55.5% of the Carnot efficiency [7]. Improvements in efficiency are proposed by utilizing materials having high values of dM/dT which are arranged in series with decreasing Curie temperatures [8]. A recent study by Vuarnoz et al. shows that the efficiency of a thermomagnetic generator can exceed the efficiency of conventional technologies, namely organic Rankine cycle (ORC), power generators, Stirling power generators and thermoelectric power generators, especially in the low exergy regime [9]. Recently, based on Fe_2P-type magnetocaloric materials, a proof of concept device was developed in order to experimentally demonstrate such a thermomagnetic energy conversion engine [10]. In addition, a simple phenomenological model was developed that allows to predict thermodynamic efficiencies of transformations based on magnetic- and heat capacity measurements [11]. Indeed, the applicability of first-order type Heusler alloys with sharp transitions magnetic and structural phase transitions was recently shown both theoretically and experimentally [5,12].

The magnetocaloric and thermomagnetic generator research fields have in common that the change of magnetization with temperature needs to be maximized. With large dM/dT, large magnetic entropy change (ΔS_M) is expected when considering the Maxwell relation (for second order transitions) [13]. Maximizing the derivative could also induce large voltages in a coil wound around the magnet according to Faraday's law thus generating thermomagnetic energy. Although the magnetic entropy change is always present, magnetocaloric applications necessitate the transition to be also dependent on an external magnetic field, for

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allowing the controlled heat release or absorption of the magnetocaloric substance, which is not a requirement for thermomagnetic energy conversion. The use of first-order phase change materials may be detrimental to the efficiency of a thermomagnetic generator because the latent heat needed to drive a first-order phase transition will be absorbed by the material during the transformation. Additionally, hysteresis effects which are usually observed in first-order type phase transitions will also lower the overall efficiency as overheating and under cooling of a material is necessary. However, heat exchangers made of cascaded stacks can increase the usable temperature range of the thermomagnetic generator and therefore increase device efficiency [9,10] like in a magnetic refrigerator. In order to prepare cascaded material stacks with specific transition temperatures, the material has to allow for precise compositional tuning and need to be machined easily. Furthermore, proper heat exchange between the materials and with the exchange fluid is also necessary to ensure an efficient operation at optimal frequencies [14–16].

To make above mentioned technologies commercially viable, the high dM/dT must occur in compounds made of abundant elements with T_C in the range of 200–800 K. In order to harvest the low exergy waste heat which are sufficiently abundant (for example heat wasted in power stations, engines, solar panels, etc.) development of new materials and/or improvement of the existing ones is necessary.

Magnetic transition metal borides are especially interesting for such applications as they show magnetic phase transitions in a wide temperature range [17,18]. These refractory borides are chemically inert and structurally stable even at elevated temperatures [19,20]. Our primary interest in MnB relates to the fact that it shows the highest magnetization of all monoboride systems [18] and a high associated large magnetovolume effect [21]. However, monoborides are difficult to prepare with high phase purity and precise composition due to the significant difference in melting temperatures of the constituents. As a result, experimental results found in literature significantly differ from each other [18,22–27]. First principle calculations on the pure compounds also highlight the important interplay between structure and composition related to the magnetic properties [20,28–31].

In this article, we focus on the tunability of the magnetic transition temperature of MnB by partial replacement of the transition metal with Fe and Co, respectively. In particular, we explore the magnetic, magnetocaloric and structural properties of the $Mn_{1-x}Co_xB$ and $Mn_{1-x}Fe_xB$ solid solutions.

Our article is structured as follows: first the experimental and theoretical procedures are described in Section II. In Section III experimental findings are shown for the pure MnB followed by results on the transition metal substitution. Theoretical calculations with comparison of the experimental results are shown in Section IV.

2. Experimental details

2.1. Sample preparation and experimental procedure

Samples were produced via arc melting on a water cooled copper plate using commercial purity Mn (99.99%), B (99%), Fe (99.9%) and Co (99.9%). Before alloying, the manganese was cleaned via subsequent arc melting and grinding steps. The evaporation of Mn and B was taken into account by additional 3 wt% and 1 wt%, respectively. Arc melting was repeated three times to ensure material homogeneity. For each consecutive melting the button was turned upside down. All investigated samples except $Mn_{0.5}Co_{0.5}B$ show homogeneous crystalline single phase in the as-cast state. In order to prepare the material $Mn_{0.5}Co_{0.5}$ B an additional annealing step at 1473 K for 2 h in a sealed quartz tube filled with Ar and water quenched was necessary to facilitate the monophase formation.

X-Ray diffraction (XRD) experiments were performed on a Stoe Stadi P instrument in transmission mode with Molybdenum $K\alpha_1$ radiation at room temperature. Rietveld refinements were performed using the Fullprof software package [32]. The stochiometry and phase purity was checked with scanning electron microscopy (SEM) (Philips XL30 FEG) in back-scatter electron diffraction (BSE) contrast and energy dispersive electron diffraction (EDX) analysis by comparing the ratio of Mn/TM. As the B is not detectable by EDX, we assume the ratio of B to be constant at 50 at.%.

Differential scanning calorimetry (DSC) measurements were performed on a Netsch DSC 200 F3 Maia® under constant N_2 flow in an Al pan covered by an Al lid with a sweeping rate of 10 K min^{-1} on a powder sample of 40 mg. The DSC and c_p sensitivity was calibrated in the desired temperature range before the measurement.

Magnetic measurements were performed on sample fragments using a Quantum Design Physical Property Measurement System (PPMS 14 T VSM) and a LakeShore vibrating sample magnetometer (VSM) with high temperature option. Magnetic isotherms were recorded in field steps of 500Oe for cooling and heating in fields up to 4T in the PPMS and 2T in the VSM. Field cooling (FC) magnetization measurements were performed with a constant ramping rate of 3 K/min under a field of 1T.

2.2. Details of the DFT model used

The electronic structure calculations were performed using the Vienna Ab Initio Simulation Package (VASP) code, based on DFT within projector augmented wave (PAW) method [33] with Perdew-Burke-Ernzerhof (PBE) parametrization. Site-based magnetic moments [34] were calculated using the Vosko-Wilk-Nusair interpolation [35] within the general gradient approximation (GGA) for the exchange-correlation potential. The minimal, 8 atoms basis cell consists of four transition metal atoms (Mn, Fe or Co) (4c) and four B atoms (4c) was used for the calculations. The lattice was fully relaxed without any imposed symmetry restriction for both non-magnetic (NM) and ferromagnetic (FM) configurations, respectively. The convergence criterion was set to 0.001 eV/Å forces. A k-point grid of $15 \times 11 \times 13$ was used for the structural relaxations. The effect of partial replacement of Mn for Fe/Co on the electronic structure was considered into the 4c crystallographic site only. Using this model, the effect of doping was simulated by the replacement of a manganese atom by iron or cobalt which represents an $x = 1/4$ compositional change in the $Mn_{1-x}(Fe/Co)_xB$ formula. The density of states (DOS) plots and magnetic properties presented in this work were calculated on a dense $(19 \times 15 \times 17)k$ grid for high accuracy. The energy convergence criterion was set to 1 eV–7 eV during the energy minimization process. Finally, the spin-orbit interaction was turned off during the calculations.

3. Experimental results and discussion

3.1. Pure MnB

The room temperature XRD measurement of MnB (see Fig. 1) shows the diffraction pattern of an orthorhombic structure (*Pnma*, space group # 62) with $a = 0.558$ *nm*, $b = 0.298$ *nm* and $c = 0.415$ *nm* in agreement with previous study [36]. Besides the main phase, a small amount of Mn_2B impurity phase (<3 wt%) was present, identified by Rietveld refinement. The same amount of minority phase was also confirmed by scanning electron microscopy in BSE mode and EDX analysis.

The temperature dependence of the spontaneous