Magnetic BiMn- α Phase Synthesis Prediction: First-principles Calculation, Thermodynamic
Modeling and Nonequilibrium Chemical Partitioning

S. H. Zhou¹, C. Liu^{2,3}, Y. X. Yao^{1,3}, Y. Du⁴, L. J. Zhang⁴, C.-Z. Wang^{1,3}, K.-M. Ho^{1,3}, M. J.
Kramer^{1,2}

¹Division of Materials Sciences and Engineering, Ames Laboratory, USDOE, USA.

²Department of Materials Science and Engineering, Iowa State University
Ames, IA 50011, USA

³Department of Physics and Astronomy, Iowa State University, Ames, IA 50011, USA

⁴State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan,
410083, PR China

Abstract

BiMn- α is promising permanent magnet. Due to its peritectic formation feature, there is a synthetic challenge to produce single BiMn- α phase. The objective of this study is to assess driving force for crystalline phase pathways under far-from-equilibrium conditions. First-principles calculations with Hubbard U correction are performed to provide a robust description of the thermodynamic behavior. The energetics associated with various degrees of the chemical partitioning are quantified to predict temperature, magnetic field, and time dependence of the phase selection. By assessing the phase transformation under the influence of the chemical partitioning, temperatures, and cooling rate from our calculations, we suggest that it is possible to synthesize the magnetic BiMn- α compound in a congruent manner by rapid solidification. The external magnetic field enhances the stability of the BiMn- α phase. The compositions of the initial compounds from these highly driven liquids can be far from equilibrium.

Keywords: First-principles calculation, Hubbard U correction, chemical partitioning, hard magnetic MnBi, composition far from equilibrium.

1. Introduction

Due to the high cost and considerably limited supplies of rare earth elements, significant attention has been paid to find potential substitutions to realize permanent magnets without rare earth elements [1, 2]. Recently, intermetallic compound manganese bismuth (BiMn- α with NiAs structure) has been shown to be a promising permanent magnetic material without rare earth elements and attracting a lot of interests due to its large uniaxial magnetic anisotropy energy and moderate Curie temperature T_c above room temperature. These desirable magnetic properties

stem from its hexagonal crystal structure with two equal axes and the third perpendicular axis of different length [3-9]. Unlike other hard magnetic materials, the coercivity of BiMn- α does not decrease with increasing temperature [10]. In this study we have assessed the thermodynamic pathways for the formation of crystalline phases under far-from-equilibrium conditions using first-principles calculations to provide a robust description of the thermodynamic behavior of undercooled liquids to predict the temperature dependent phase selection under magnetic field.

The phase diagram of the Bi–Mn system has been experimentally determined [11-16] as can be seen from the review by Massalski et al. [17]. Two-liquid separation behavior at temperatures higher than 1508K was evaluated using thermal analysis by Siebe [12]. The liquidus boundaries up to 1000K were consistently determined by several researchers [13-15] from pure Bi to about 39.2 at.% Mn using differential thermal analysis (DTA). Two compounds, i.e. the low temperature stable phase BiMn- α and the high temperature stable phase BiMn- β , were found in the Bi-Mn system [13-15]. An eutectic reaction $\text{liq} \leftrightarrow (\text{Bi}) + \text{BiMn-}\alpha$ and a peritectic reaction $\text{liq} + \text{Mn-cbcc} \leftrightarrow \text{BiMn-}\beta$ (at TP2) were confirmed at 537K and 719K, respectively [13-15]. The formation of the magnetic compound BiMn- α is transformed from BiMn- β at TP1=628 K [13, 14]. Chen [16] studied the Bi–Mn phase diagram using DTA, X-ray diffraction, metallography and electron microprobe analysis (EPMA), and showed that the high-temperature phase BiMn- β with chemical atomic ratio 1:1.08 (symbolized as BiMn_{1.08}- β in following text) is separated from BiMn- α compound by a peritectic phase transformation $\text{liq} + \text{BiMn}_{1.08}\text{-}\beta \leftrightarrow \text{BiMn-}\alpha$ at 628K. The eutectoid reaction $\text{BiMn}_{1.08}\text{-}\beta \leftrightarrow \text{BiMn-}\alpha + \text{Mn-cbcc}$ is at 613K. Pirich et al.[15] investigated the phase equilibria of the Bi–Mn system near the eutectic region (95–100 at.% Bi) by means of differential scanning calorimetry (DSC), chemical, spectrophotometric absorbance and energy dispersive X-ray spectrometry and reported a eutectic $\text{liq} \leftrightarrow \text{Bi-rho} + \text{BiMn-}\alpha$ temperature of 538.1K and a eutectic composition of

Fig. 1. The Bi-Mn phase diagram resulting from the present model using the parameters in Table 5 and comparing with the experimental data.

2.69 $\pm$ 0.08 at.% Mn. The peritectic reaction BiMn_{1.08}- β +liq $\leftrightarrow$ BiMn- α temperature measured by Koyama et al.[18] is 632K which is a little higher than 628 K[13, 14, 16]. Pure BiMn- α phase cannot be cast since that additional Mn is required to compensate for Mn precipitation during solidification [19]. The experimental data are summarized in Fig. 1.

The enthalpy of formation of the BiMn- α phase at 298K was measured using high-temperature direct synthesis calorimetry by Shchukarev et al.[20] in Fig. 2. Thermodynamic activities of the liquid phase were determined by Weinstein and Elliott [21] and Katayama et al.[22], respectively, using an electromotive force (EMF) technique. The data from both references [21, 22] are in good agreement with each other.

Thermodynamic modeling of the binary Bi-Mn was developed by Wang et al. [23] and Oikawa et al.[24]. The significant differences between the two studies [23, 24] lie in Gibbs free energy descriptions for both liquid and compound. Wang et al. [23] described liquid with miscibility gap at high temperature while in the work by Oikawa [24], the two-liquid separation is at undercooled liquid temperature range. The difference for the liquid modeling in the two studies [23, 24] arises from the modeling strategy. The experimental activities of the liquid phase from ref.[21, 22] were employed to determine the thermodynamic parameters by Oikawa et al.[24] but ignored by Wang et al.[23]. Therefore we believe that the model parameters of liquid by Oikawa et al.[24] are reliable. For the BiMn- α and BiMn_{1.08}- β compounds, the magnetic contribution to Gibbs energy was considered by Oikawa et al.[24] but disregard by Wang et al.[23]. As the dash-lines shown in Fig. 2, three parameter sets with considering the magnetic contributions by Oikawa et al.[24] produce the different enthalpies of formation for both BiMn- α and BiMn_{1.08}- β phases. Therefore, although we believe that thermodynamic modeling by Oikawa

Fig. 2. Enthalpy of formation at 298K, calculated using the parameters in Table 5 in comparison with the first-principles data and experimental data and modeling results (dash-line) by Oikawa et al. [24].

et al. [24] is more reliable, the enthalpy of formation for the BiMn- α phase should be calculated based on the first-principles calculations. This is the first issue we will address in this paper.

Many researchers have studied heat treatment effects on the BiMn- α compound in external magnetic fields [25-33]. The magnetic field effect on the T_c of the BiMn- α phase was reported by Liu et al. [30] on the basis of magnetization measurements up to 10 T. They showed that the magnetic field increases the stability of the BiMn- α phase. Koyama et al.[8] found that BiMn- α decomposition temperature T_{p1} increases in a rate of 2 K/T by the high field differential thermal analysis (HFDTA) for magnetic field B up to 14 T. The HFDTA experiments [31, 32] with magnetic field B up to 45 T showed that T_{p1} is increased by 84 K and reaches the temperature very close to the peritectic temperature T_{p2} as shown in Fig. 3. It was found that T_{p2} is also increased slightly by applying magnetic field. As mentioned above, the Bi-Mn phase diagram varies with increasing magnetic fields due to the increasing stability of the BiMn- α phase so that it is possible to find a way to synthesize it. The Bi-Mn phase diagrams under external magnetic fields were calculated by Mitsui et al. [32] based on CALPHAD approach in which the energy contribution of the external magnetic field to the Gibbs free energy was calculated using mean field theory. As second issue, therefore it is useful to determine the magnetic field dependent enthalpy of formation of the BiMn- α phase based on first-principles calculations using density functional theory (DFT).

DFT calculations have been performed for the BiMn- α phase by many scientists [34-40]. The calculated magnetic moments show significant differences i.e. $3.52 \mu_B$ [34], $4.01 \mu_B$ [35], $3.50 \mu_B$ [36], and $3.49 \mu_B$ [37], respectively. The calculation values are different from $3.9 \mu_B$ which is the estimated magnetic moment at 0 K from experimental data [41]. The lattice parameters calculated in refs.[34-37] also deviate from experimental results [16]. To understand

Fig. 3. Magnetic field dependence of the peritectic reaction temperatures for the BiMn- α and BiMn_{1.08}- β compounds.

the properties of the BiMn- α phase, Zarkevich et al.[38] compared the DFT calculations results with and without the Hubbard U correction, and found that including the electron correlations through DFT+U results in larger values of the lattice parameters. Antropov et al.[39] studied the spin reorientation in BiMn- α using the local spin density approximation (LSDA)+U calculations. They treated U as an adjustable parameter and found that good agreement with experimental observations [10, 42] can be achieved for a larger value of U. Shanavas et al.[40] studied the electronic structure and lattice dynamics in the BiMn- α compound using first-principles DFT and tight-binding calculations and showed that the cell volume of the BiMn- α were underestimated with DFT. BY including an adjustable U (1–2 eV) [40], the magnetic moments, unit cell volume and lattice parameter ‘c’ calculated using generalized gradient approximation

Fig. 4. Effect of Coulomb repulsion U on the structure and magnetism calculated from GGA+U through structural optimizations for the MnBi- α compound.

(GGA) [43] are in better agreement with the experimental data as shown in Fig. 4, while those calculated using LSDA+U are too high in comparison with the experimental data. These results indicate that GGA+U calculation is more reliable. The third objective of the present work is to perform GGA+U calculations to understand the stability of the BiMn- α from the energy point of view.

Rapid solidification for synthesizing single phase of BiMn- α has been well studied [6, 44-51]. The amorphous phase was reported in Bi₄₉Mn₅₁ ribbon [44] and Mn₅₀Bi₅₀ ribbon [46] produced by melt-spun with tangential wheel speed (TWS) over 50 m/s. Zhang et al.[47] found BiMn- α in Mn_xBi_{100-x} ($x=48, 50, 55$ and 60) melt-spun ribbons (MSR) and confirmed that the segregation of Mn-cbcc from liquid can be restrained by increasing TWS. In the Mn₅₂Bi₄₈ MSR, more than 95 wt. % BiMn- α phase was identified by Kharel et al. [49]. The MSR of the Mn_xBi_{100-x} ($x=40-60$) alloys obtained with TWS=50m/s demonstrate that the peritectic reaction tends to be inhibited and thus the liquid phase experiences significant undercooling before solidification occurs [50]. The Mn₅₅Bi₄₅ MSR with relative slow TWS=20m/s [51] reveals the presence of multiple phases BiMn- α , Mn₃Bi, Bi-rho and Mn-cbcc. The experimental investigations [6, 44-51] indicate that the formation of the BiMn- α phase is cooling rate dependent. The primary Mn-cbcc phase can be suppressed and peritectic reactions can be broken so that the MnBi- α and MnBi_{1.08}- β phase are able to form directly from the undercooled liquid. Heat treatment after melt-spun results in significant increase of the MnBi- α phase in MSR [6, 44-50]. The fourth objective of the present work is to tackle the thermodynamic behavior of undercooled liquids to predict cooling rate dependent phase selections and to understand the pathway for the formation of the single MnBi- α phase.

In the work reported here, we address each of these four issues and provide a comprehensive picture regarding to the phase formation in the Bi-Mn system. More generally, by incorporating first-principles calculations into our semi-empirical approach, we bring the clarity to the overall thermodynamic description of this system which allows us to analyze further the possible phase transformations at the far-from-equilibrium conditions.

2. First-principles calculation

To determinate the Gibbs free energy of formation for the intermediate phases, the energies of the intermetallic phase BiMn- α and the references Mn-cbcc and Bi-rho at T=0K were

calculated by means Vienna *ab initio* simulation package (VASP) [52-54] employing projector augmented wave method [54, 55] and PBE-GGA (Perdew-Burke-Ernzerhof GGA) [43, 56] with high precision and 500 eV plane-wave energy cutoff. A Γ -centered $16 \times 16 \times 10$ Monkhorst-Pack k-point grid with was applied for BiMn- α , a $24 \times 24 \times 24$ grid for Mn-cbcc and a $16 \times 16 \times 16$ grid for Bi-rho structures, respectively. The unit cell shape and the internal atomic coordinates are fully relaxed for the stable end-member BiMn (end-member will be described in section 3), and only the cell volumes for those unstable end-members BiBi and MnMn of the BiMn- α compound as listed in Table 1 are relaxed.

Table 1 A summary of results from the first-principles calculations.

Phase Φ	prototype	formula	U eV	Space group	First-principles eV/atom ΔH_f^Φ kJ/mol		Lattice parameter a (Å) c (Å)		V _{cell} Å ³
<i>Bi</i>	As (rho)	<i>Bi</i>	0	R-3mh	-3.90715	0	4.5951	12.0441	220.23
			0		-8.96382	0	7.3975	---	311.63
			0.75		-8.03154	0	7.3947	---	311.27
<i>Mn-cbcc</i>	Mn (cbcc)	<i>Mn</i>	1.00	<i>I</i> -43m	-7.72106	0	7.3938	---	311.16
			1.25		-7.41073	0	7.3956	---	311.38
			1.50		-7.10077	0	7.4101	---	313.22
			2.00		-6.584	0	7.4924	---	323.77
		<i>BiBi</i>			-3.76528	9.74	4.5235	8.0265	142.25
		<i>BiMn</i>	0		-6.15894	26.95	4.3135	5.7069	91.96
		<i>MnMn</i>			-8.25009	68.86	3.5408	4.5132	48.95
		<i>BiMn</i>	0.75		-5.92163	4.60	4.3457	5.7912	94.72
<i>BiMn-α</i>	NiAs	<i>BiMn</i>	1.00	<i>P</i> 6 ₃ / <i>mmc</i>	-5.85006	-3.47	4.3551	5.8393	95.92
		<i>MnMn</i>	1.00		-7.01831	67.80	3.5197	4.5146	48.87
		<i>BiMn</i>	1.25		-5.78283	-11.95	4.3605	5.9033	97.21
		<i>BiMn</i>	1.50		-5.71853	-20.70	4.3597	5.9798	98.43
		<i>BiMn</i>	2.00		-5.59968	-34.14	4.3407	6.1695	100.67
		<i>MnMn</i>	2.00		-6.42811	15.099	2.4774	8.0074	42.55
<i>Mn₇₅Bi₂₅</i>	fcc-SQS16	<i>Mn₇₅Bi₂₅</i>	0	<i>Fm</i> -3m	-6.78116	87.344	---	---	---
<i>Mn₅₀Bi₅₀</i>		<i>Mn₅₀Bi₅₀</i>			-5.00314	136.03	---	---	---
<i>Mn₇₅Bi₂₅</i>	bcc-SQS16	<i>Mn₇₅Bi₂₅</i>	0	<i>Im</i> -3m	-6.73375	91.92	---	---	---
<i>Mn₅₀Bi₅₀</i>		<i>Mn₅₀Bi₅₀</i>			-5.06309	130.25	---	---	---

The enthalpy of formation, ΔH_f^Φ can be calculated as the difference between the energy of the compound, E_{TOT}^Φ , and linear combination of the pure element reference state energies, E_{Bi}^{rho} and E_{Mn}^{cbcc} ,

$$\Delta H_f^\Phi = E_{TOT}^\Phi - x_{Bi}^\Phi E_{Bi}^{rho} - x_{Mn}^\Phi E_{Mn}^{cbcc} \quad (1)$$

where x_i^Φ is the mole fraction of component i in the Φ phase. The calculated enthalpies of formation of the compounds are listed in Table 1. The enthalpy of formation for BiMn- α has positive value 26.95kJ/mol, indicating that formation of BiMn- α phase is energetically not favorable which is contradictory with experiment. Contradictions to experimental observation are also reported in ref. [16, 34-37, 41] for magnetic moment and lattice parameters. To get correct results, DFT+U [57, 58] calculation as done in refs.[38-40] was applied in this work for calculating the energy of the BiMn- α phase. The energies and lattice constants calculated through structural optimizations for different values of effective U parameter on Mn d-electrons are listed in Table 1. The formation energy ΔH_f^α , μ_m , lattice

Fig. 5. Effect of Coulomb repulsion U on the enthalpy of formation for the MnBi- α compound calculated from GGA+U through structural optimizations.

parameters, and unit cell volume V_{cell} for BiMn- α as the function of the on-site Coulomb interaction parameter U interpolated from the points obtained from DFT+U calculations are plotted in Figs. 4 and 5. Experimental data of ΔH_f^α , μ_m , lattice parameters 'a' and 'c', and V_{cell} are also listed in Table 2. By comparing the experimental ΔH_f^α in Table 2 with the calculated

Table 2 Determining the enthalpy of formation of the BiMn- α phase

U(ev/f.u.)	ΔH_f^α (kJ/mol)	μ_M (μ_B)	a (Å)	c (Å)	V_{cell} (Å ³)
1.191	-9.8	3.77	4.35913	5.88813	96.89
1.217	-10.5	3.9	4.35953	5.89508	97.03
2.142	-39.28	3.97	4.34905	6.113	100.12
Exp.	-9.8 [20]	3.9 [41]	4.285 [16]	6.113[16]	97.21[16]

curve shown in Fig. 5, U is determined to be 1.191 eV (see the cross point in Fig. 5. With U=1.191 eV, the corresponding μ_m , lattice parameters, and V_{cell} values were determined using the interpolated curves in Fig. 4 and listed in Table 2. Using same procedure to match the

experimental data of μ_m , lattice parameters, and V_{cell} with the calculation results respectively, different U vales and the properties corresponding to these U vales can be determined as listed in Table 2. It should be noted that there is no cross point between the lattice parameter ‘a’ and curve in Fig. 4(b) which is same as the report by Shanavas et al.[40]. In comparison, the

Fig. 6. Enthalpies of mixing of the bcc and fcc at 298K, calculated using the parameters in Table 5 in comparison with the first-principles data.

Fig. 7. The magnetic field dependent enthalpy of formation for the BiMn- α compound calculated using First-principles approach.

calculated results based on the experimental data $\mu_m=3.9\mu_B$ seem reasonable so that U and ΔH_f^α are determined to be 1.217 eV and -10.5 kJ/mol, respectively.

To evaluate the Gibbs free energy of the fcc and bcc solution phases, their enthalpies of mixing were calculated with first-principles approach, using 16-atom Quasirandom Structures (SQSs) [59, 60]. The concept of SQS was proposed by Zunger et al.[59] to mimic a random solution phase by reproducing the pair and multiple-body correlations using a small-sized supercell. The fcc [60] and bcc [61] SQS solution structures were employed in this work. The energetics of the fcc- and bcc-SQS at compositions of $x_{\text{Mn}} = 0.5$ and 0.75 were computed using the GGA with VASP [54]. A Γ -centered $10 \times 8 \times 6$ Monkhorst-Pack k-point grid was applied for the calculations. Similar to the unstable end-members of the compound, we only relax the cell volumes of the fcc- and bcc-SQS. The calculated enthalpy of mixing for the bcc and fcc phases using Eq. 1 are listed in Table 1 and plotted in Fig. 6.

The stability of the BiMn- α is affected by magnetic field. Due to the different magnetic effectiveness for the BiMn- α and BiMn_{1.08}- β phases, the Tp1 increases in the rate of 2 K/T [8] while the slope for the Tp2 is very small as shown in Fig. 3. Therefore the electronic structure calculations were carried out for the BiMn- α phase in the ferromagnetic state using full potential linearized augmented plane-wave (FP-LAPW) method with the local spin density approximation [62] as implemented in the Elk code package [63]. The muffin-tin radii of 2.4 Å were chosen for Mn and 2.8 Å for Bi. The lattice parameter of 8.088, 11.546 Å for ‘a’ and ‘c’, respectively, were used for the calculations. The Brillouin zone integrations were performed with a (14x14x10) k-point mesh and $R_{mt}K_{max}=7$ is employed. Variant strength of magnetic fields parallel to the c axis was applied throughout the entire unit cell. The calculated results of the external magnetic field dependence of total energies are listed in Table 3 and plotted in Fig. 7. The result indicates that the external magnetic field makes the enthalpy of formation of the BiMn- α phase more negative.

Table 3 First-principles calculated magnetic field dependent energy.

B Tesla	Energy	
	meV/formula	J/mol of atom
0	0	0
0.858	-0.14889	-7.18
1.715	-0.28824	-13.91
2.573	-0.50107	-24.17
3.431	-0.64177	-30.96
4.288	-0.85459	-41.23
5.146	-0.99937	-48.21
6.003	-1.19992	-57.89
6.861	-1.35013	-65.13
7.719	-1.55612	-75.07
8.576	-1.69952	-81.99
9.434	-1.84699	-89.10

3. Thermodynamic descriptions

Thermodynamic models in the present work are based on the sublattice models developed by Sundman and Agren[64]. As defined in Table 4, the total Gibbs free energy for any phase, Φ , is generally given by the sum of three contributions,

$$G_m^\Phi = {}^{ref}G_m^\Phi + {}^{id}G_m^\Phi + {}^{xs}G_m^\Phi \quad (2)$$

where the subscript, m , indicates that all terms are molar quantities. The first term in Eq. 2 is the

Table 4 Summary of the thermodynamic models used for the Bi-Mn binary system with the total Gibbs free energy $G_m^\Phi = {}^{ref}G_m^\Phi + {}^{id}G_m^\Phi + {}^{xs}G_m^\Phi$ (p and q are the subscript value of the formulation).

Phase ϕ	Prototype	Method (Formulation)	Model
Liquid	---	Solution model	$^{ref}G_m^\Phi = \sum_{i=Bi,Mn} x_i^\circ G_i^\Phi + ^{mag}G_m^\Phi$
Mn-fcc	Cu		$^{id}G_m^\Phi = RT \sum_{i=Bi,Mn} x_i \ln x_i$
Mn-bcc	W		$^{xs}G_m^\Phi = x_{Bi}x_{Mn} \sum_{j=0}^n {}^jL_{Bi,Mn}^\Phi (x_{Bi} - x_{Mn})^j$
Two-sublattice model (Bi,Mn) _p (Bi,Mn) _q			
BiMn- α	NiAs	(Bi,Mn) ₁ (Ni,Mn) ₁	$^{ref}G_m^\Phi = \sum_{i=Bi,Mn} y_i^I \sum_{j=Bi,Mn} y_j^{II} {}^\circ G_{i:j}^\Phi$ ${}^\circ G_{i:j}^\Phi = {}^\circ G_i^{ref} + {}^\circ G_j^{ref} + \Delta G_{i:j}^\Phi + ^{mag}G_{i:j}^\Phi$ $= {}^\circ G_i^{ref} + {}^\circ G_j^{ref} + a_{i:j}^\Phi + b_{i:j}^\Phi T + ^{mag}G_{i:j}^\Phi$ $^{id}G_m^\Phi = RT \sum_{i=Bi,Mn} (y_i^I \ln y_i^I + y_i^{II} \ln y_i^{II})$
BiMn _{1.08} - β	---	(Bi,Mn) ₁ (Bi,Mn) _{1.08}	$^{xs}G_m^\Phi = y_{Bi}^I y_{Mn}^I \sum_{i=Bi,Mn} y_i^{II} \sum_{k=0}^k {}^kL_{Bi,Mn:i}^\Phi (y_{Bi}^I - y_{Mn}^I)^k$ $+ y_{Bi}^{II} y_{Mn}^{II} \sum_{i=Bi,Mn} y_i^I \sum_{k=0}^k {}^kL_{i:Bi,Mn}^\Phi (y_{Bi}^{II} - y_{Mn}^{II})^k$

sum of occupancy-weighted sublattice end-member contributions, while the second and third terms are the ideal and excess parts of the Gibbs free energy of mixing, respectively.

3.1 Liquid, fcc and bcc phases

Liquid, fcc, and bcc terminal solution phases are treated as substitutional solutions with the solution model as listed in Table 4. The Gibbs free energy ${}^\circ G_i^\Phi$ of the pure element i with the structure Φ are from the database by Dinsdale [65]. The magnetic contribution, ${}^{mag}G_m^\Phi$, is discussed in section 3.3, while ${}^jL_{Bi,Mn}^\Phi$ is the j^{th} interaction parameter between component Bi and Mn, expressed as ${}^j a^\Phi + {}^j b^\Phi T$, with ${}^j a^\Phi$ and ${}^j b^\Phi$ being model parameters to be evaluated in this work.

3.2 Intermetallic phase

The BiMn- α and BiMn_{1.08}- β phases are described using the two-sublattice model, $(Bi,Mn)_p(Bi,Mn)_q$ as listed in Table 4 in which $Bi_p Bi_q$, $Bi_p Mn_q$, $Mn_p Bi_q$ and $Mn_p Mn_q$ are the end-members for each phase. The Gibbs free energy ${}^\circ G_{i:j}^\Phi$ of the end-member $i:j$ is modeled in Table 4 where ${}^\circ G_i^{ref}$ and ${}^\circ G_j^{ref}$ ($i, j = Bi$ and Mn) of the elements Bi and Mn from the database by Dinsdale[65]. $\Delta G_{i:j}^\Phi$ is the Gibbs energy of formation of the end-member $i:j$ with no magnetic

contribution included. $^{xs}G_m^\Phi$ is the excess Gibbs energy, expressed in the Redlich-Kister polynomial [66] in Table 4 in which $^kL^\Phi$ is the k^{th} interaction parameter and assumed to be zero in this work. y^I and y^{II} are the site fractions in the first and second sublattices, respectively, and $^{mag}G_{i;j}^\Phi$ is the magnetic contribution [67] to Gibbs free energy as described in following section.

Table 5 Thermodynamic parameters for the Gibbs free energy in Table 4.

Phase Φ	Parameter	Value of parameter (J/mol)	$T_c(K)$	$\beta(\mu_B)$
Liquid	$^0L_{Bi,Mn}^{liq}$	21696-25.958T[24]	0	0
	$^1L_{Bi,Mn}^{liq}$	-22328+7.4855T[24]	0	0
	$^2L_{Bi,Mn}^{liq}$	10.614T[24]	0	0
Mn-fcc	$^0L_{Bi,Mn}^{fcc}$	513124	0	0
	$^1L_{Bi,Mn}^{fcc}$	156578.7	0	0
Mn-bcc	$^0L_{Bi,Mn}^{bcc}$	490984	0	0
	$^1L_{Bi,Mn}^{bcc}$	61509.3	0	0
BiMn- α	$\Delta G_{Bi:Bi}^\alpha$	19544	0	0
	$\Delta G_{Bi:Mn}^\alpha$	-13033.5-19.09958 B+(12.644-	720[33]	3.9[33]
	$\Delta G_{Mn:Bi}^\alpha$	0.03076 B+1.28939*10 ⁻⁴ B ²)T		
	$\Delta G_{Mn:Mn}^\alpha$	135607.9	0	0
BiMn _{1.08} - β	$\Delta G_{Bi:Bi}^\beta$	26864.6	0	0
	$\Delta G_{Bi:Mn}^\beta$	-7016+(1.337-2.85714*10 ⁻⁵ B-	470[33]	1.7[33]
	$\Delta G_{Mn:Bi}^\beta$	2.21429*10 ⁻⁵ B ²)T		
	$\Delta G_{Mn:Mn}^\beta$	147571.1	0	0
	$\Delta G_{Mn:Mn}^\beta$	147571.1	0	0

3.3 Magnetic energy

The magnetic energy contribution, $^{mag}G_m^\Phi$ [67] of the terminal Mn or a compound to Gibbs free energy is considered in this work, and expressed as:

$$^{mag}G_m^\Phi = RT \ln(\beta^\Phi + 1) f(\tau^\Phi) = ^{mag}H_m^\Phi - T^{mag}S_m^\Phi, \quad (3)$$

where β^Φ is a quantity related to the total magnetic entropy and is set equal to the Bohr magnetic moment per mole of atom. τ^Φ is defined as T/T_c^Φ and T_c^Φ is the Curie temperature.

For the solution phase, T_c^Φ and β^Φ are described as:

$$T_c^\Phi = x_A {}^0T_{cA}^\Phi + x_B {}^0T_{cB}^\Phi + x_A x_B \sum_{j=0}^n {}^jL_{T(A,B)}^\Phi (x_A - x_B)^j \quad (4)$$

$$\beta^\Phi = x_A {}^0\beta_A^\Phi + x_B {}^0\beta_B^\Phi + x_A x_B \sum_{j=0}^n {}^jL_{\beta(A,B)}^\Phi (x_A - x_B)^j \quad (5)$$

where ${}^0T_{ci}^\Phi$ and ${}^0\beta_i^\Phi$ are from end-member as listed in Table 5. For the BiMn- α and BiMn_{1.08}- β phases, ${}^0T_{ci}^\Phi$ and ${}^0\beta_i^\Phi$ [33] are listed in Table 5 while those for the terminal Mn-fcc, -bcc and -cbcc phases can be found in pure element database [65]. Lastly, ${}^jL_{T(A,B)}^\Phi$ and ${}^jL_{\beta(A,B)}^\Phi$ are the magnetic interaction parameters between the elements A and B.

4. Model parameter evaluation and phase diagram calculation

There are 8 parameters for Gibbs free energy of formation (ΔG) and 7 parameters for binary interaction parameters (0L) in our model the Bi-Mn system (see Table 5). The parameter evaluation was performed using experimental data combined with first-principles results and was carried out in an iterative manner as described briefly below.

The liquid parameters evaluated by Oikawa et al. [24] based on the thermodynamic activities [21, 22] were employed in this work and listed in Table 5. The parameters of the bcc and fcc phases were determined with the first-principles data in Table 1. The calculated results are plotted in Fig. 6.

With the absence of the relevant data, the parameters $\Delta G_{i:i}^\alpha$ (i=Bi or Mn) for the unstable end-members of the BiMn- α phase in Table 4 are treated as constants $a_{i:i}^\alpha$ and determined using the first-principles calculated enthalpies of formation in Table 1. For the stable end-member, the coefficients $a_{Bi:Mn}^\alpha$ in Table 4 is evaluated from the first-principles data -10.5kJ/mol in Table 2 while the parameter $b_{Bi:Mn}^\alpha$ in Table 4 was determined with the upper limit TP1=628 K [13, 14, 16]. The parameters $a_{Bi:Mn}^\beta$ and $b_{Bi:Mn}^\beta$ of the BiMn_{1.08}- β phase were determined with experimental upper [13] and lower [16] limits of the decomposition temperatures and listed in Table 5. Because there are no data available, the parameters $a_{Bi:Bi}^\beta$ and $a_{Mn:Mn}^\beta$ were estimated from $a_{Bi:Mn}^\beta$, $a_{Bi:Mn}^\alpha$ and $a_{i:i}^\alpha$ (i=Bi and Mn) as following. We calculated the difference $\Delta a_{Bi:Mn}$ between $a_{Bi:Mn}^\beta$ and $a_{Bi:Mn}^\alpha$ ($\Delta a_{Bi:Mn} = a_{Bi:Mn}^\beta - a_{Bi:Mn}^\alpha$). The parameter $a_{i:i}^\beta$ then was approximately calculated by $a_{i:i}^\beta = a_{i:i}^\alpha + \Delta a_{Bi:Mn}$ and listed in Table 5. The parameter $a_{Mn:Bi}^\beta$ is assumed to be equal to that of $a_{Mn:Mn}^\beta$. $b_{Mn:Bi}^\beta$ and $b_{i:i}^\beta$ are assumed to be zero. The improvements for the parameters $a_{i:i}^\beta$ and $a_{Mn:Bi}^\beta$ are necessary when the first-principles calculation becomes

available for the $\text{BiMn}_{1.08}\text{-}\beta$ phase. With the thermodynamic parameters in Table 5, the Bi-Mn phase diagram is calculated and plotted in Fig. 1. The enthalpies of formation for the Bi-Mn system and enthalpies of mixing for the bcc and fcc phases calculated using the parameters in Table 5 are plotted in Fig. 2 and Fig. 6, respectively. The accuracy of this calculation arises from the utilization of both first-principles calculations and experiments to clarify the relative stability of the intermetallic phases.

The experimental data in Fig. 3 show the magnetic field B dependence of the peritectic reaction temperature indicating the parameters $a_{\text{Bi:Mn}}^{\alpha}$ and $b_{\text{Bi:Mn}}^{\alpha}$ are magnetic field dependent. The first-principles calculated enthalpy of formation for the $\text{BiMn-}\alpha$ compound is plotted in Fig. 7 with which the parameters $a_{\text{Bi:Mn}}^{\alpha}$ as function of the magnetic field B is estimated as $a_{\text{Bi:Mn}}^{\alpha} (= -13033.5 - 19.09958 \cdot B)$. The parameter $b_{\text{Bi:Mn}}^{\alpha} (= 12.644 - 0.03076 \cdot B + 1.28939 \cdot 10^{-4} \cdot B^2)$ was evaluated with the magnetic field B dependent peritectic reaction ($\text{liq} + \text{BiMn}_{1.08}\text{-}\beta \rightarrow \text{BiMn-}\alpha$) temperatures in Fig. 3. By assuming $a_{\text{Bi:Mn}}^{\beta}$ being constant, the parameter $b_{\text{Bi:Mn}}^{\beta}$ as function of the magnetic field B was also evaluated with the experimental data in Fig. 3 and summarized in Table 5. The invariant reactions $\text{liq} + \text{Mn-cbcc} \rightarrow \text{BiMn}_{1.08}\text{-}\beta$ and $\text{liq} + \text{BiMn}_{1.08}\text{-}\beta \rightarrow \text{BiMn-}\alpha$ calculated as function of the magnetic field B using the parameters in Table 5 are plotted in Fig.

Fig. 8. The calculated phase diagram with considering the magnetic field (a) $B=18\text{T}$ in comparison with experimental data and (b) varying from 0 to 55T.

3. We can see that there is difference between the calculated results and experimental data [31, 32] at B=0. This is due to the parameter $b_{Bi:Mn}^\alpha$ evaluated on basis of the experimental data TP1=628 K[13, 14, 16] while the experimental data TP1 by Koyama et al.[18, 31, 32] is 632K. The phase diagram under magnetic field B=18 T is calculated in Fig. 8(a) with the experimental data [31] showing a good agreement. The equilibrium phase transformation vs. T, x_{Mn} and magnetic field B is plotted in Fig. 8(b) indicating that the formation of the BiMn_{1.08}- β compound can be avoided by increasing the magnetic field up to 47.5T with very slow cooling rate. In following section, we will analyze the phase transformation possibility for getting single BiMn- α phase with varying high cooling rate from energy point of view.

5. Chemical Partitioning-Temperature-Phase Transformation (CPTPT) calculation

To understand the varying degrees of chemical partitioning, the Gibbs free energies for the liquid and BiMn- α phases at T=600K are plotted in Fig.

9. The equilibrium compositions $^l x_{equ}^{liq}$ and x_{equ}^α bound positive driving force for the formation of the α phase on its left side. This range includes two important regimes where (i) partitionless solidification may be observed and (ii) some degree of chemical partitioning is required in the composition range. The partitionless solidification, i.e. the compositions between x_0^l and x_0^2 is defined by the criterion $G_m^{liq} = G_m^\alpha$ bounding the partitionless range (PL-range) in Fig. 9, over which $^0 G_m^{liq} > ^0 G_m^\alpha$ such that the liquid

Fig. 9. The Gibbs free energies of the liquid and BiMn- α phases at 600K computed with the parameters in Table 5.

phase may transform directly into the solid phase in a diffusionless manner. Thus, this range represents the "zero diffusion time" limit. Over a range of temperatures, these limiting compositions define so called T_0 (solid line) curves as plotted in Fig. 10(a), in which as previously suggested [68], the T_0 curves provide a practical limit for partitionless crystallization. For the liquid phase, the spinodal curve is also plotted in Fig. 10(a) to indicate its spontaneous decomposition range. The T_0 curves as well as the spinodal curve were calculated as function of

the magnetic field B as shown in Fig. 10(b) which indicates the relative stabilities of the phases vary with the magnetic field B in the diffusionless manner i.e. unlimited high cooling rate.

Fig. 10. The liquidus T_L and T_0 curves (a) magnetic field $B=40$; (b) T_0 as function of the magnetic field B computed using the parameters in Table 5.

The partitioning range labeled P-range in Fig. 9 between $^l x_{equ}^{liq}$ and x_0^l is the composition range that requires diffusion time for crystallization. From an energy standpoint, only the BC-range in Fig. 9 for a given liquid composition as indicated $x_{Mn}^{liq} = x_l$ is allowed to crystallize. BC-range is determined by cross points (at $^i x_{BC}^\alpha$) between the tangent line of liquid at $x_{Mn}^{liq} = x_l$ and G_m^α curve. The crystallization of the BiMn- α phase with a composition in the BC-Range from x_l liquid will reduce the system energy.

Focusing now on the composition P-range between $^l x_{equ}^{liq}$ and x_0^l and considering the required diffusion time, we recognize that the limits, i.e., T_L (liquidus)-dashed lines and T_0 solid-lines in Fig. 10(a), represent only the two-terminal cases. A continuum should exist between them, as determined by the degree of chemical partitioning, which we described previously [69], using a parameter, η , being defined as the degree of chemical partitioning

$$\eta = (\mu_{Mn}^{liq} - {}^0\mu_{Mn}^{liq}) / ({}^{eq}\mu_{Mn}^{liq} - {}^0\mu_{Mn}^{liq}) \quad (6)$$

This parameter is inversely related to chemical supersaturation as described in Ref.[69] in the liquid phase, as shown in Fig. 9, for a liquid composition $x_{Mn}^{liq} = x_l$. μ_{Mn}^{liq} , ${}^0\mu_{Mn}^{liq}$, and ${}^{eq}\mu_{Mn}^{liq}$ are the chemical potentials at the compositions x_l , x_0^l and $^l x_{equ}^{liq}$ of the liquid phase, respectively.

For a given temperature, x_l starts from x_0^l and ends at ${}^l x_{equ}^{liq}$ associating variation of μ_{Mn}^{liq} from ${}^0 \mu_{Mn}^{liq}$ to ${}^{eq} \mu_{Mn}^{liq}$ so that η varies from 0 to 1 indicating the increasing minimum diffusional burden that accompanies the solidification transition for the range in liquid composition between ${}^l x_{equ}^{liq}$ and x_0^l . As shown in Fig. 11(a), the α phase formation composition range from liquid with the composition represented by liq_{start}^α for each η varying from 0 to 1 is calculated at 614K. The curve liq_{start}^α means the composition to start crystallization with respect to a “ η ” associated with a particular degree of constraint on the level of supersaturation that can be relieved by diffusion and thus is called as "the effective liquidus".

Fig. 11. The α crystallization from liquid with the degree of chemical partitioning η varying from 0 to 1 (a) at 614K and (b) the crystallization surface showing the influence of initial supersaturation indicated by the degree of chemical partitioning η on the effective liquidus with the surface varying from T_0 to T_L as well as the liquid separation and (c) the computed driving force for solidification of the BiMn- α and BiMn_{1.08}- β phases from a liquid of composition $x_{Mn} = 0.5$ as computed using the parameters in Table 5 under magnetic field $B=40T$.

Over a range of temperature, the full crystallizations surface i.e. "the effective liquidus" for the crystal phases as well as the liquid separation comprised of these level curves are plotted in Fig. 11(b) with $B=40$ T. The parameter, η , can be viewed, alternatively, as a time-scale associated with the required diffusional relaxation where $\eta=1$ corresponds to the infinite-time

limit and $\eta=0$ corresponds to the zero-time limit. Thus, the effective crystallization surface that applies to any real process (i.e., one with a finite cooling rate) would be indicated by the appropriate η value. Further examination of Fig. 10(b) and Fig. 11(b) reveals three more important features. First, if η is on zero side, i.e., very high cooling rate, both BiMn- α and BiMn_{1.08}- β phases can directly form from the liquid in a congruent manner. Second, eutectic like reaction $\text{liq} \rightarrow \text{BiMn-}\alpha + \text{BiMn}_{1.08}\text{-}\beta$ is possible with $x_{\text{Mn}} = 0.5$ with both high magnetic field and η . The solidification can be in following order: single BiMn- α phase formation in congruent manner $\rightarrow$ eutectic reaction $\rightarrow$ peritectic reaction dependent on the magnetic field and η . Third, the possible composition range for a compound likely becomes larger with decreasing η , i.e., composition of a compound can be far from equilibrium.

As shown in Fig. 8(b), the formation of the BiMn_{1.08}- β phase is possible to be restricted by increasing the magnetic field up to 47.45T at equilibrium state i.e. with very slow cooling rate. The Mn-cbcc, however, cannot be prevented as shown in Fig. 8. The BiMn- α and BiMn_{1.08}- β compounds are possible to be synthesized directly from liquid by very high cooling rate i.e. diffusionless manner as shown in Fig. 10 to avoid the formation of the Mn-cbcc phase. In this case, the BiMn_{1.08}- β phase is prior to BiMn- α to form at zero or low external magnetic field. With increasing the external magnetic field, the BiMn- α phase is stabilized and possible to form directly from the liquid phase around $B=70$ T as shown in Fig. 10(b). In practice, $B=70$ T is not a trivial magnetic field to achieve. To understand possible phase transformation pathway, the driving force is a key in predicting and controlling phase competition/selection during rapid solidification process. Fig. 11(c) shows the driving force as a function of temperature for the BiMn- α and BiMn_{1.08}- β phases at $x_{\text{Mn}}=0.5$ and $B=40\text{T}$, indicating that the BiMn_{1.08}- β and BiMn- α phases are allowed to solidify from liquid at 788 and 780K, respectively. Below 733K, the reaction $\text{BiMn}_{1.08}\text{-}\beta \rightarrow \text{BiMn-}\alpha$ is imperative due to BiMn_{1.08}- β being less stable than BiMn- α . The chemical partitioning calculations in Fig. 11(b) show that BiMn- α and BiMn_{1.08}- β are allowed to form from liquid with high cooling rate and high external magnetic field. At slow cooling rate approximate to $\eta=1$ in Fig. 11(b), Mn-cbcc is the primary phase. According to the results in Figs. 10-11, the BiMn_{1.08}- β is the primary phase under low external magnetic field. Therefore, to synthesize high percentage BiMn- α phase, the high cooling rate and high magnetic field should be applied. Once BiMn_{1.08}- β prior to BiMn- α forms from liquid at high cooling rate

for the Bi-50at.%Mn alloy, the heat treatment for the reaction $\text{BiMn}_{1.08}\beta \leftrightarrow \text{BiMn}\alpha$ at 613K should be implemented to ensure that $\text{BiMn}_{1.08}\beta$ transforms into $\text{BiMn}\alpha$ completely from driving force point of view.

6. Conclusion

To get the enthalpy of formation for the compound $\text{BiMn}\alpha$, first-principles calculations plus Hubbard U correction were employed in this work. The external magnetic field effect for the energy of the $\text{BiMn}\alpha$ phase was also determined using the first-principles calculations. The enthalpies of mixing of the solid solution (fcc and bcc) phases were calculated from the first-principles approach using 16-atom SQSs. The thermodynamic parameters required for the phase diagram calculations were evaluated on the basis of the first-principles results and experimental data from the literature. The calculated phase diagram indicates that the $\text{BiMn}_{1.08}\beta$ phase can be suppressed in the high magnetic field. The CPTPT calculation indicates that the compounds $\text{BiMn}\alpha$ and $\text{BiMn}_{1.08}\beta$ are able to form in congruent manner and eutectic reaction with increasing cooling rate and magnetic field. The compositions of the compounds from these highly driven liquids can be far from equilibrium. The single hard magnetic $\text{BiMn}\alpha$ phase can be obtained with high cooling rate from liquid under high magnetic field. Once the formation of $\text{BiMn}_{1.08}\beta$ is prior to that of $\text{BiMn}\alpha$, heat treatment around 613K is necessary to get high percentage $\text{BiMn}\alpha$ phase. These results demonstrate that CPTPT calculations can be a powerful tool for guiding the alloy design.

ACKNOWLEDGMENT

The magnetic alloy development was supported by the US Department of Energy (DOE) Advanced Research Projects Agency-Energy (ARPA-E) under Contract No. 11/CJ000/09/03. Computational methods development was supported by the US Department of Energy, Basic Energy Sciences, Division of Materials Science and Engineering. Ames Laboratory is operated for the US DOE by Iowa State University under contract #DE-AC02-07CH11358.

References

- [1] J.M.D. Coey. *Scr. Mater.* 67 (2012) 524-529.
- [2] N. Jones. *Nature* 472 (2011) 22-23.
- [3] B.W. Roberts. *Phys. Rev.* 104 (1956) 607-616.
- [4] J.B. Yang, K. Kamaraju, W.B. Yelon, W.J. James, Q. Cai, A. Bollero. *Appl. Phys. Lett.* 79 (2001) 1846.
- [5] S.S. Jaswal, J.X. Shen, R.D. Kirby, D.J. Sellmyer. *Appl. Phys. Lett.* 75 (1994) 6346.

- [6] S. Saha, R.T. Obermyer, B.J. Zande, V.K. Chandhok, S. Simizu, S.G. Sankar, J.A. Horton. *J. Appl. Phys.* 91 (2002) 8525-8527.
- [7] J.B. Yang, W.B. Yelon, W.J. James, Q. Cai, S. Roy, N. Ali. *J. Appl. Phys.* 91 (2002) 7866-7868.
- [8] K. Koyama, T. Onogi, Y. Mitsui, Y. Nakamori, S.I. Orimo, K. Watanabe. *Mater. Trans., JIM* 48 (2007) 2414-2418.
- [9] X. Li, Z. Ren, G. Cao, Y. Fautrelle, C. Esling. *Acta Mater.* 59 (2011) 6297-6307.
- [10] J.B. Yang, Y.B. Yang, X.G. Chen, X.B. Ma, J.Z. Han, Y.C. Yang, S. Guo, A.R. Yan, Q.Z. Huang, M.M. Wu, D.F. Chen. *Appl. Phys. Lett.* 99 (2011) 082505.
- [11] E. Bekier. *Int. Ztsch. Metallog.* 7 (1915) 83.
- [12] P. Siebe. *Z. Anorg. Allg. Chem.* 108 (1919) 161-183.
- [13] A.U. Seybolt, H. Hansen, B.W. Roberts, P. Yurcisin. *Trans. Amer. Inst. Min. Metal. Eng.* 206 (1956) 606-610.
- [14] E. Wachtel, R. Damm. *Z. Metallk.* 54 (1963) 693-697.
- [15] R.G. Pirich, G. Busch, W. Poit, D.J. Larson. *Metall. Trans. A* 11 (1980) 193-194.
- [16] T. Chen. *J. Appl. Phys.* 45 (1974) 2358-2360.
- [17] H.O. T.B. Massalski, P.R. Subramanian, L. Kacprzak. *Binary Alloy Phase Diagrams*, ASM International, Materials Park, OH, 1990.
- [18] K. Koyama, Y. Mitsui, E.S. Choi, Y. Ikehara, E.C. Palm, K. Watanabe. *J. Alloys Compd.* 509 (2011) L78-L80.
- [19] J. Cui, J.-P. Choi, E. Polikarpov, M.E. Bowden, W. Xie, G. Li, Z. Nie, N. Zarkevich, M.J. Kramer, D. Johnson. *Acta Mater.* 79 (2014) 374-381.
- [20] S. Shchukarev, T.A. Stolyarova, M.P. Morozova. *Zh. Obshch. Khim.* 31 (1961) 1773-&.
- [21] M. Weinstein, J.F. Elliott. *J. Electrochem. Soc.* 110 (1963) 792-798.
- [22] I. Katayama, S. Matsushima, Z. Kozuka. *Mater. Trans., JIM* 31 (1990) 789-792.
- [23] Y.E. Kalay, I. Kalay, J. Hwang, P.M. Voyles, M.J. Kramer. *Acta Mater.* 60 (2012) 994-1003.
- [24] K. Oikawa, Y. Mitsui, K. Koyama, K. Anzai. *Mater. Trans., JIM* 52 (2011) 2032-2039.
- [25] H. Morikawa, K. Sassa, S. Asai. *Mater. Trans., JIM* 39 (1998) 814-818.
- [26] H. Yasuda, I. Ohnaka, Y. Yamamoto, K. Tokieda, K. Kishio. *Mater. Trans., JIM* 44 (2003) 2207-2212.
- [27] Q. Wang, C.S. Lou, T. Liu, N. Wei, C.J. Wang, J.C. He. *J. Phys. D: Appl. Phys.* 42 (2009).
- [28] X. Li, Z.M. Ren, Y. Fautrelle, K. Deng. *J. Magn. Magn. Mater.* 321 (2009) 2694-2700.
- [29] C.S. Lou, Q.A. Wang, T. Liu, N. Wei, C.J. Wang, J.C. He. *J. Alloys Compd.* 505 (2010) 96-100.
- [30] Y.S. Liu, J.C. Zhang, S.X. Cao, G.Q. Jia, X.Y. Zhang, Z.M. Ren, X. Li, C. Jing, K. Deng. *Solid State Commun.* 138 (2006) 104-109.
- [31] Y. Mitsui, K. Koyama, K. Watanabe. *Mater. Trans., JIM* 54 (2013) 242-245.
- [32] Y. Mitsui, K. Oikawa, K. Koyama, K. Watanabe. *J. Alloys Compd.* 577 (2013) 315-319.
- [33] K.H.J. Buschow. *Rep. Prog. Phys.* 40 (1977) 1179-1256.
- [34] R. Coehoorn, R.A. Degroot. *J. Phys. F: Met. Phys.* 15 (1985) 2135-2144.
- [35] P. Ravindran, A. Delin, P. James, B. Johansson, J.M. Wills, R. Ahuja, O. Eriksson. *Phys. Rev. B* 59 (1999) 15680-15693.
- [36] M.-F. Li, T. Ariizumi, K. Koyanagi, S. Suzuki. *Jpn. J. Appl. Phys., Part 1* 46 (2007) 3455-3462.

- [37] J.B. Yang, W.B. Yelon, W.J. James, Q. Cai, M. Kornecki, S. Roy, N. Ali, P. l'Heritier. J. Phys. Condens. Matter 14 (2002) 6509-6519.
- [38] N.A. Zarkevich, L.-L. Wang, D.D. Johnson. APL Mater. 2 (2014) 032103.
- [39] V.P. Antropov, V.N. Antonov, L.V. Bekenov, A. Kutepov, G. Kotliar. Phys. Rev. B 90 (2014) 054404.
- [40] K.V. Shanavas, D. Parker, D.J. Singh. Sci. Rep. 4 (2014).
- [41] R.R. Heikes. Phys. Rev. 99 (1955) 446-447.
- [42] K. Keiichi, M. Yoshifuru, W. Kazuo. Sci. Technol. Adv. Mater. 9 (2008) 024204.
- [43] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais. Phys. Rev. B 46 (1992) 6671-6687.
- [44] X. Guo, A. Zaluska, Z. Altounian, J.O. Stromolsen. J. Mater. Res. 5 (1990) 2646-2651.
- [45] K. Suzuki, X. Wu, V. Ly, T. Shoji, A. Kato, A. Manabe. J. Appl. Phys. 111 (2012) 07E303.
- [46] Y.B. Yang, X.G. Chen, R. Wu, J.Z. Wei, X.B. Ma, J.Z. Han, H.L. Du, S.Q. Liu, C.S. Wang, Y.C. Yang, Y. Zhang, J.B. Yang. J. Appl. Phys. 111 (2012).
- [47] D.T. Zhang, W.T. Geng, M. Yue, W.Q. Liu, J.X. Zhang, J.A. Sundararajan, Y. Qiang. J. Magn. Magn. Mater. 324 (2012) 1877-1890.
- [48] Y.B. Yang, X.G. Chen, S. Guo, A.R. Yan, Q.Z. Huang, M.M. Wu, D.F. Chen, Y.C. Yang, J.B. Yang. J. Magn. Magn. Mater. 330 (2013) 106-110.
- [49] P. Kharel, V.R. Shah, X.Z. Li, W.Y. Zhang, R. Skomski, J.E. Shield, D.J. Sellmyer. J. Phys. D: Appl. Phys. 46 (2013) 095003.
- [50] T. Saito, R. Nishimura, D. Nishio-Hamane. J. Magn. Magn. Mater. 349 (2014) 9-14.
- [51] S. Kavita, U.M.R. Seelam, D. Prabhu, R. Gopalan. J. Magn. Magn. Mater. 377 (2015) 485-489.
- [52] G. Kresse, J. Hafner. Phys. Rev. B 49 (1994) 14251-14269.
- [53] G. Kresse, J. Furthmüller. Phys. Rev. B 54 (1996) 11169-11186.
- [54] G. Kresse, D. Joubert. Phys. Rev. B 59 (1999) 1758-1775.
- [55] P.E. Blöchl. Phys. Rev. B 50 (1994) 17953-17979.
- [56] J.P. Perdew, K. Burke, M. Ernzerhof. Phys. Rev. Lett. 77 (1996) 3865-3868.
- [57] V.I. Anisimov, J. Zaanen, O.K. Andersen. Phys. Rev. B 44 (1991) 943-954.
- [58] V.I. Anisimov, I.V. Solovyev, M.A. Korotin, M.T. Czyżyk, G.A. Sawatzky. Phys. Rev. B 48 (1993) 16929-16934.
- [59] A. Zunger, S.H. Wei, L.G. Ferreira, J.E. Bernard. Phys. Rev. Lett. 65 (1990) 353-356.
- [60] S.H. Wei, L.G. Ferreira, J.E. Bernard, A. Zunger. Phys. Rev. B 42 (1990) 9622-9649.
- [61] C. Jiang, C. Wolverton, J. Sofo, L.-Q. Chen, Z.-K. Liu. Phys. Rev. B 69 (2004) 214202.
- [62] W. Kohn, L.J. Sham. Phys. Rev. 140 (1965) A1133-A1138.
- [63] Code. <http://elk.sourceforge.net/> (n.d.).
- [64] B. Sundman, J. Agren. J. Phy. Chem Solids 42 (1981) 297-301.
- [65] A.T. Dinsdale. CALPHAD 15 (1991) 317-425.
- [66] O. Redlich, A.T. Kister. Ind. and Eng. Chem. 40 (1948) 345-348.
- [67] M. Hillert, M. Jarl. CALPHAD 2 (1978) 227-238.
- [68] S.H. Zhou, R.E. Napolitano. Acta Mater. 54 (2006) 831-840.
- [69] S.H. Zhou, R.E. Napolitano. Phys. Rev. B 78 (2008).

Table 1 A summary of results from the first-principles calculations.

Phase Φ	prototype	formula	U eV	Space group	First-principles		Lattice parameter		V_{cell}
					eV/atom	ΔH_f^ϕ kJ/mol	a (Å)	c (Å)	Å ³
<i>Bi</i>	As (rho)	<i>Bi</i>	0	R-3mh	-3.90715	0	4.5951	12.0441	220.23
<i>Mn-cbcc</i>	Mn (cbcc)	<i>Mn</i>	0	<i>I-43m</i>	-8.96382	0	7.3975	---	311.63
			0.75		-8.03154	0	7.3947	---	311.27
			1.00		-7.72106	0	7.3938	---	311.16
			1.25		-7.41073	0	7.3956	---	311.38
			1.50		-7.10077	0	7.4101	---	313.22
			2.00		-6.584	0	7.4924	---	323.77
<i>BiMn-α</i>	NiAs	<i>BiBi</i>		<i>P6₃/mmc</i>	-3.76528	9.74	4.5235	8.0265	142.25
		<i>BiMn</i>	0		-6.15894	26.95	4.3135	5.7069	91.96
		<i>MnMn</i>			-8.25009	68.86	3.5408	4.5132	48.95
		<i>BiMn</i>	0.75		-5.92163	4.60	4.3457	5.7912	94.72
		<i>BiMn</i>	1.00		-5.85006	-3.47	4.3551	5.8393	95.92
		<i>MnMn</i>			-7.01831	67.80	3.5197	4.5146	48.87
		<i>BiMn</i>	1.25		-5.78283	-11.95	4.3605	5.9033	97.21
		<i>BiMn</i>	1.50		-5.71853	-20.70	4.3597	5.9798	98.43
		<i>BiMn</i>	2.00		-5.59968	-34.14	4.3407	6.1695	100.67
		<i>MnMn</i>			-6.42811	15.099	2.4774	8.0074	42.55
<i>Mn₇₅Bi₂₅</i>	fcc-SQS16	<i>Mn₇₅Bi₂₅</i>	0	<i>Fm-3m</i>	-6.78116	87.344	---	---	---
<i>Mn₅₀Bi₅₀</i>		<i>Mn₅₀Bi₅₀</i>			-5.00314	136.03	---	---	---
<i>Mn₇₅Bi₂₅</i>	bcc-SQS16	<i>Mn₇₅Bi₂₅</i>	0	<i>Im-3m</i>	-6.73375	91.92	---	---	---
<i>Mn₅₀Bi₅₀</i>		<i>Mn₅₀Bi₅₀</i>			-5.06309	130.25	---	---	---

Table 2 Determining the enthalpy of formation of the *BiMn- α* phase

U(ev/f.u.)	ΔH_f^α (kJ/mol)	μ_M (μ_B)	a ($\text{\AA}$)	c ($\text{\AA}$)	V_{cell} ($\text{\AA}^3$)
1.191	-9.8	3.77	4.35913	5.88813	96.89
1.217	-10.5	3.9	4.35953	5.89508	97.03
2.142	-39.28	3.97	4.34905	6.113	100.12
Exp.	-9.8 [20]	3.9 [41]	4.285 [16]	6.113[16]	97.21[16]

Table 3 First-principles calculated magnetic field dependent energy.

B Tesla	Energy meV/formula	J/mol of atom
0	0	0
0.858	-0.14889	-7.18
1.715	-0.28824	-13.91
2.573	-0.50107	-24.17
3.431	-0.64177	-30.96
4.288	-0.85459	-41.23
5.146	-0.99937	-48.21
6.003	-1.19992	-57.89
6.861	-1.35013	-65.13
7.719	-1.55612	-75.07
8.576	-1.69952	-81.99
9.434	-1.84699	-89.10

Table 4 Summary of the thermodynamic models used for the Bi-Mn binary system with the total Gibbs free energy $G_m^\Phi = {}^{ref}G_m^\Phi + {}^{id}G_m^\Phi + {}^{xs}G_m^\Phi$ (p and q are the subscript value of the formulation).

Phase ϕ	Prototype	Method (Formulation)	Model
Liquid	---		$^{ref}G_m^\Phi = \sum_{i=Bi,Mn} x_i \circ G_i^\Phi + ^{mag}G_m^\Phi$
Mn-fcc	Cu	Solution model	$^{id}G_m^\Phi = RT \sum_{i=Bi,Mn} x_i \ln x_i$
Mn-bcc	W		$^{xs}G_m^\Phi = x_{Bi}x_{Mn} \sum_{j=0}^n {}^jL_{Bi,Mn}^\Phi (x_{Bi} - x_{Mn})^j$
Two-sublattice model (Bi,Mn) _p (Bi,Mn) _q			
BiMn- α	NiAs	(Bi,Mn) ₁ (Ni,Mn) ₁	$^{ref}G_m^\Phi = \sum_{i=Bi,Mn} y_i^I \sum_{j=Bi,Mn} y_j^{II} \circ G_{i:j}^\Phi$ $\circ G_{i:j}^\Phi = \circ G_i^{ref} + \circ G_j^{ref} + \Delta G_{i:j}^\Phi + ^{mag}G_{i:j}^\Phi$ $= \circ G_i^{ref} + \circ G_j^{ref} + a_{i:j}^\Phi + b_{i:j}^\Phi T + ^{mag}G_{i:j}^\Phi$ $^{id}G_m^\Phi = RT \sum_{i=Bi,Mn} (y_i^I \ln y_i^I + y_i^{II} \ln y_i^{II})$
BiMn _{1.08} - β	---	(Bi,Mn) ₁ (Bi,Mn) _{1.08}	$^{xs}G_m^\Phi = y_{Bi}^I y_{Mn}^I \sum_{i=Bi,Mn} y_i^{II} \sum_{k=0}^k L_{Bi,Mn:i}^\Phi (y_{Bi}^I - y_{Mn}^I)^k$ $+ y_{Bi}^{II} y_{Mn}^{II} \sum_{i=Bi,Mn} y_i^I \sum_{k=0}^k L_{i:Bi,Mn}^\Phi (y_{Bi}^{II} - y_{Mn}^{II})^k$

Table 5 Thermodynamic parameters for the Gibbs free energy in Table 4.

Phase Φ	Parameter	Value of parameter (J/mol)	$T_c(K)$	$\beta(\mu_B)$
Liquid	${}^0L_{Bi,Mn}^{liq}$	21696-25.958T[24]	0	0
	${}^1L_{Bi,Mn}^{liq}$	-22328+7.4855T[24]	0	0
	${}^2L_{Bi,Mn}^{liq}$	10.614T[24]	0	0
Mn-fcc	${}^0L_{Bi,Mn}^{fcc}$	513124	0	0
	${}^1L_{Bi,Mn}^{fcc}$	156578.7	0	0
Mn-bcc	${}^0L_{Bi,Mn}^{bcc}$	490984	0	0
	${}^1L_{Bi,Mn}^{bcc}$	61509.3	0	0
BiMn- α	$\Delta G_{Bi:Bi}^\alpha$	19544	0	0
	$\Delta G_{Bi:Mn}^\alpha$	-13033.5-19.09958 B+(12.644-	720[33]	3.9[33]
	$\Delta G_{Mn:Bi}^\alpha$	0.03076 B+1.28939*10 ⁻⁴ B ²)T		
	$\Delta G_{Mn:Mn}^\alpha$	135607.9	0	0
	$\Delta G_{Bi:Bi}^\beta$	26864.6	0	0
BiMn _{1.08} - β	$\Delta G_{Bi:Mn}^\beta$	-7016+(1.337-2.85714*10 ⁻⁵ B-	470[33]	1.7[33]
		2.21429*10 ⁻⁵ B ²)T		
	$\Delta G_{Mn:Bi}^\beta$	147571.1	0	0
	$\Delta G_{Mn:Mn}^\beta$	147571.1	0	0