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Effect of isoelectronic substitution on magnetic properties of $Ni_2Mn(GaB)$ Heusler alloys

Bhoj Raj Gautam, Igor Dubenko, Arjun Kumar Pathak, Shane Stadler and Naushad Ali

Department of Physics, Southern Illinois University, Carbondale, IL 62901, USA

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Abstract

We have studied the structural and magnetic properties of $Ni_2MnGa_{1-x}B_x$ Heusler alloys with $0 \leqslant x \leqslant 0.25$ using x-ray diffraction, thermal expansion, electrical resistivity, and magnetization measurements. The magnetization measurements were made within the temperature interval of 5–400 K and at applied magnetic field of 0–5 T. The samples with low B concentrations ($x < 0.05$) were found to be of the cubic $L2_1$ phase at 300 K. A martensitic phase along with the cubic $L2_1$ phase appears for $x \geqslant 0.05$, and the amount of the martensitic phase was found to increase with increasing x. The critical concentration of the boron substitution (within which Heusler phases exist) was found to be around $x = 0.1$. The cubic cell parameter was observed to decrease with increasing x in the interval $0 \leqslant x \leqslant 0.1$. The alloys were ferromagnetically ordered at 5 K and the saturation magnetization (M_S) was found to decrease with increasing boron concentration. The Curie temperatures (T_C) and martensitic transition temperatures (T_M) for the alloys with $0 \leqslant x \leqslant 0.25$ have been determined and a phase (T–x) diagram has been constructed. T_M increases rapidly and T_C decreases slowly with increasing B concentration in the interval $0 \leqslant x \leqslant 0.1$. The dependence of the phase transition temperatures and magnetization on B concentration is discussed.

1. Introduction

Ferromagnetic Ni–Mn–Ga Heusler alloys have attracted interest due to magnetic shape memory effects and large value of magnetic entropy changes at the magnetostructural transitions [1, 2]. The Ni_2MnGa Heusler alloy is ferromagnetic below $T_C = 376$ K and undergoes a structural transition from an austenitic phase (AP) with cubic $L2_1$ structure to a martensitic phase (MP) at $T_M \cong 202$ K [3]. The magnetic moment of this alloy resides on the Mn atoms. The indirect exchange interaction gives rise to the ferromagnetism in Ni_2MnGa Heusler alloys [4, 5]. It has been established that the magnetic and structural properties of Ni_2MnGa Heusler alloys strongly depend on the stoichiometry and chemical composition [6–10]. The merging of T_C and T_M is a favorable condition to achieve magnetic shape memory and giant magnetocaloric effects [11, 12]. Band structure calculation and neutron diffraction measurements suggest that the structural phase transition in Ni–Mn–Ga Heusler alloys is driven by a band Jahn–Teller effect [13, 14]. Recently, studies of the effects of elemental substitution at the Ga site in Ni_2MnGa have been augmented [15–20]. The substitution of Ti, Co, and Fe for Ga in Ni_2MnGa Heusler alloys increases the T_M [17–19]. The opposite effect is observed when the Ga in Ni_2MnGa is replaced by Ge, Si, and Tb [17–20]. The T_M was found to increase with increasing conduction electron per atom (e/A ratio) for Ni–Mn–Ga–Ti alloys [20]. However, in Ni–Mn–Ga–Ge alloys the T_M is reported to decrease with an increase of e/A ratio [21].

The T_M in the Ni_2MnGa Heusler alloys observed to be decreasing linearly with increasing Al concentration for isoelectronic substitution of Ga by Al [22]. The substitution of Ga by In in Ni–Mn–Ga decreases both the T_M and T_C [20]. Thus, the e/A ratio is not the only factor affecting the phase transition temperature in the Ni–Mn–Ga based Heusler alloys [23]. Therefore, to ascertain the relative contribution of different factors affecting the phase transition temperatures in the Ni–Mn–Ga, more studies are required.

In this paper we report the influence of isoelectronic substitution of B for Ga on the structural and magnetic properties of Ni_2MnGa Heusler alloys. One can expect that the

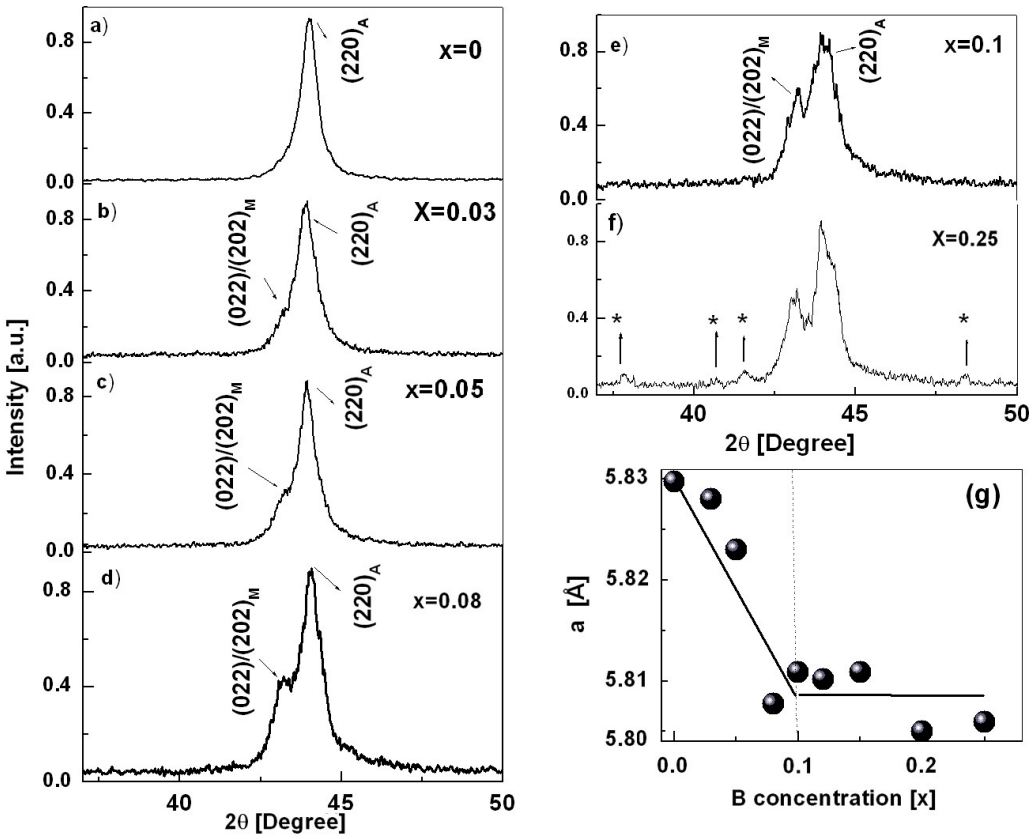

Figure 1. (a)–(f) X-ray diffraction patterns of $Ni_2MnGa_{1-x}B_x$ with $x = 0$, 0.03, 0.05, 0.08, 0.01, and 0.25, respectively. (g) Crystal cell parameter versus boron concentration x.

substitution of B results in a decrease of the crystal cell volume. The existence of Ni_2MnB Heusler alloy has been predicted and the ground state electronic structure, magnetic properties and their response to the pressure in the Ni_2MnB alloy has been studied theoretically [24].

2. Sample preparation and measurements

Polycrystalline $Ni_2MnGa_{1-x}B_x$ samples (with $x = 0$, 0.03, 0.05, 0.08, 0.1, 0.12, 0.15, 0.2, and 0.25) were prepared using standard arc-melting methods from 4 N purity metallic elements Ni, Mn, Ga, and B in an argon atmosphere. To compensate the loss of Mn during the melting process, an additional 2% of the stoichiometric Mn mass was added to the starting material masses. To obtain homogeneity, the samples were re-melted three or four times and annealed at 850 °C for 72 h in a vacuum furnace.

The phase compositions and crystal structures were determined from conventional powder x-ray diffraction methods using Cu Kα radiation and Bragg–Brentano geometry at room temperature. The temperature and field dependences of magnetization were studied using a superconducting quantum interference device (SQUID) magnetometer within the temperature range of 5–400 K, and at external magnetic fields up to 5 T. Thermal expansion measurements were made using a high resolution capacitance dilatometry method in the temperature range of (90–300) K [25]. The electrical resistivity was measured using the standard four-probe technique in zero and 5 T magnetic fields and with a heating or cooling rate of 3 K min^{-1}. The saturation magnetizations were determined by extrapolating the linear parts of M $(1/H)$ curves to infinite magnetic field.

3. Result and discussion

Room temperature x-ray data show (figure 1) that the $Ni_2MnGa_{1-x}B_x$ Heusler alloys are in single (austenitic) or in mixed (austenitic and martensitic) phases depending on the boron concentration in the interval $0 \leqslant x \leqslant 0.1$. The parent Ni_2MnGa alloy is a single phase compound with cubic $L2_1$ crystal structure. Starting from the B concentration $x = 0.03$, tetragonal peaks from martensitic phase are observed (see figure 1). It can be concluded from the comparison of intensities of cubic and tetragonal peaks that as the value of x increases the amount of the tetragonal phase increases as shown in figures 1(a)–(e). Starting from $x = 0.1$ additional peaks of an undetermined phase were observed and became significant for the larger values of x (see figure 1(f) for $x = 0.25$). The increasing amount of the tetragonal phase with increasing B concentration can be due to decreasing the difference between the temperature of martensitic transition and room temperature. The x-ray phase diagram (figure 1(g)) shows that the cubic cell parameter (a) decreases with increasing x for the alloys with $x \leqslant 0.1$, and it

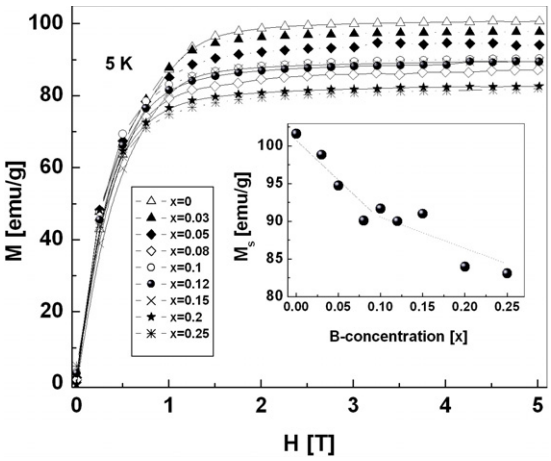

Figure 2. Field variation of magnetization $M(H)$ at 5 K. Inset: the variation of the saturation magnetization at 5 K (M_S) with x.

remains almost same for $x > 0.1$. The reason for the decrease of the cubic cell parameter is the smaller radius of the B atom as compared to that of the Ga atom. From the x-ray diffraction patterns and (a–x) phase diagram (figure 1), it is clear that the B can substitute for Ga in the parent Ni_2MnGa alloy only within the concentration interval of $0 \leqslant x \leqslant 0.1$. Hence, $x \cong 0.1$ is the critical concentration (x_C) of B, beyond which the alloys are in mixed phases. The critical concentration of B substitution for Ga ($x_C \cong 0.1$) is found to be less than that of B substitution for Mn ($x_C \cong 0.25$) in Ni_2MnGa [26].

The field dependences of the magnetization $M(H)$ measured at 5 K for the different compositions are shown in figure 2. All the compounds were found to exhibit ferromagnetic behavior at 5 K. From the $M(H)$ data shown in figure 2, one can observe that the increasing B concentration decreases the magnetic hardness of the alloys. The saturation field is observed to decrease for increasing B concentration (see figure 2). The magnetization for an applied external magnetic field of 5 T at 5 K decreases with the boron concentration.

The inset of figure 2 shows that the saturation magnetization (M_S) at 5 K decreases almost linearly with increasing x. This decrease of M_S is most likely due to the decrease of the lattice constant. Theoretical and experimental studies show that the ground state magnetic moment decreases with increase of ambient pressure [24, 27, 28]. We have observed that M_S decreases with increase in B concentration. The application of pressure results in the decrease of the lattice parameter and thereby Mn–Mn distance. The B substitution also decreases the lattice parameter and the Mn–Mn distance. The decrease of the Mn–Mn distance changes the hybridization of Mn states and results in the decrease of Mn magnetic moment. In this sense our result is consistent with the theoretical studies of pressure dependence on magnetic moment.

Representative temperature dependence of the magnetization $M(T)$ curves of $Ni_2MnGa_{1-x}B_x$ are shown in figure 3 for $x = 0$, 0.03, 0.05, and 0.15. From the $M(T)$ data, two types of $M(T)$ were observed. The alloys with $x \leqslant 0.03$ are characterized by three phase transition temperatures: T_C, T_P, and T_M upon cooling. With decreasing temperature from 400 K, the magnetization of the alloys increases abruptly, indicating a magnetic transition at T_C. For further cooling there is a small dip-like peak (around 260 K for the alloys with $x = 0.3$) described as a pre-martensitic transition (T_P). Finally, a sharp decrease in magnetization below 300 K is observed. This transition is described as the martensitic transition (MT). The martensitic transition of Heusler alloys is accompanied by an abrupt decrease in magnetization at low applied magnetic field, about 0.1 T. The martensitic transition is observed due to the structural change (from high symmetry austenite to low symmetry martensite) and thereby increasing magnetic anisotropy with reduction in the number of easy axes. All of the alloys with $x \geqslant 0.05$ show two transitions T_C and T_M. The pre-martensitic transition T_P is not observed for the alloys with $x \geqslant 0.05$.

The electrical resistivity curves (presented in figure 4) for the alloys with $x = 0.03$ and 0.05 show typical metallic behavior in the increase of resistivity with increasing temperature below T_M. The step-like feature at T_M can be seen clearly for both alloys. The thermal hysteresis of resistivity about 15 K, observed for the alloy with $x = 0.05$, signifies the first order nature of the martensitic transition. A noticeable slope change in the resistivity around 285 K for alloys with $x = 0.03$ indicates the pre-martensitic transition. One can see a change in slope of the resistivity curve at higher temperature (around 385 K), indicating the Curie temperature.

The inset of figure 4 shows a thermal expansion ($\Delta L/L$) curve for the compound with $x = 0.03$. The step-like variation of the thermal expansion data at T_M confirms the first order nature of the transition.

The variation of the phase transition temperature in the $Ni_2MnGa_{1-x}B_x$ system with boron concentration evaluated from our results is given in a (T–x) phase diagram (see figure 5). The increase of boron content results in an increase of T_M and T_P, while T_C slightly decreases for the low concentration interval ($0 \leqslant x \leqslant 0.1$). The rate of increase of T_M with respect to boron concentration is about 900 K/x within the concentration interval 0–0.1. T_P increases from 270 to 279 K when the boron concentration increases from 0 to 0.03. T_C decreases from 390 to 377 K ($\cong$160 K/x) in the concentration interval of 0–0.1. T_M increases slowly (at the rate of 70 K/x), and T_C remains almost the same at 374 K for the alloys with $x > 0.1$. T_P was observed only for the alloys with $x = 0$ and 0.03. The substitution of Mn by B in Ni_2MnGa (see [25]) results in different behavior of T_M and T_P as compared to that of Ga by B. In $Ni_2Mn_{1-x}B_xGa$ T_M remains almost constant for lower concentration of B ($x \leqslant 0.08$) and decreases rapidly for higher B concentration. The decrease of T_C in $Ni_2Mn_{1-x}B_xGa$ alloys ($\cong$450 K/x) is more rapid than that in $Ni_2MnGa_{1-x}B_x$($\cong$160 K/x).

The isoelectronic substitution of Ga by In in Ni_2MnGa Heusler alloys (see [20]) results in the decrease of all three phase transition temperatures: T_C, T_P and T_M. In $Ni_2MnGa_{1-x}In_x$, T_C, T_P and T_M decrease at the rate of 400 K/x, 550 K/x and 100 K/x respectively. Since B and Ga are isoelectronic, the substitution of Ga with B does not change the conduction electron density (e/A). Therefore,

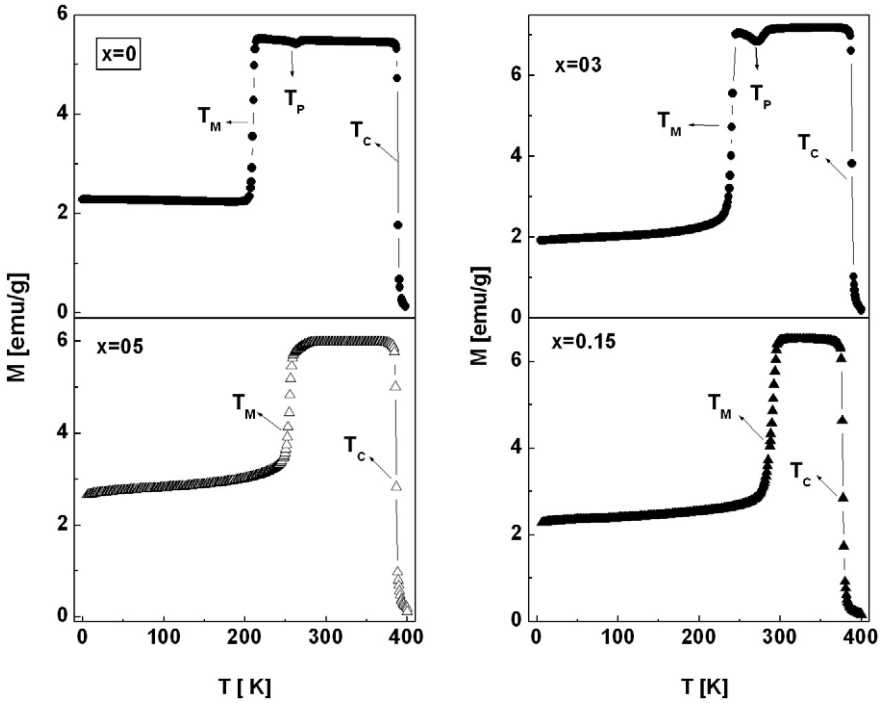

Figure 3. Temperature variation of magnetization of $Ni_2MnGa_{1-x}B_x$ for $x = 0$, 0.03, 0.05, and 0.15 at $H = 0.01$ T.

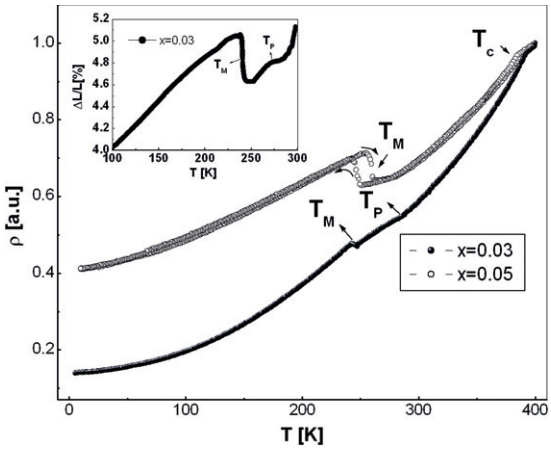

Figure 4. Variation of resistivity of $Ni_2MnGa_{1-x}B_x$ with temperature for $x = 0.03$, and 0.05. Inset: thermal expansion for the alloy with $x = 0.03$.

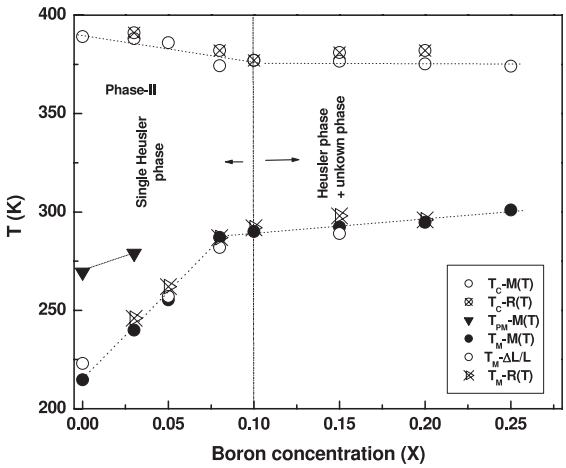

Figure 5. $(T–x)$ phase diagram of $Ni_2MnGa_{1-x}B_x$.

in $Ni_2MnGa_{1-x}B_x$ Heusler alloys, variation of the transition temperatures T_C, T_P and T_M can not be explained on the basis of conduction electron concentration. In the $Ni_2MnGa_{1-x}In_x$ system, the cell parameter of the austenitic phase increases with increasing In concentration at 300 K (see [20]). In the present study, the cell parameter of the austenitic phase is decreasing for increasing B concentration. The increase or decrease of the cell parameter is due to the different size of B, Ga, and In atoms. In the In doped system the cell parameter increases due to substitution of the smaller Ga atom (atomic radius 1.81 Å) by a larger In atom (atomic radius 2.00 Å). But for the B doped alloys the tendency is opposite. In these alloys the larger Ga atom is substituted by smaller B atom (atomic radius 1.17 Å). The different behavior of T_M and T_P for In and B substitution for Ga in Ni_2MnGa alloys indicates that the atomic size factor has a dominant role for the phase stability in these systems.

According to a band Jahn–Teller mechanism of distortion in Heusler alloys [13, 14], the cubic austenitic phase can lose stability when the Fermi level is located near the maximum of the d-electron density of states. It has been shown in [14] from band structure calculations that the total energy of the austenitic phase is at a minimum with $a = 5.85$ Å for Ni_2MnGa Heusler alloys. Thus the reduction in the cell parameter of $Ni_2MnGa_{1-x}B_x$ (see figure 1(f)) can result in a decrease of the stability of the austenitic phase due to a shift of the cell parameter of the cubic phase from optimum

value. Such changes in the cell parameter can also increase the martensitic transition temperature by driving the Fermi level toward the maximum of the d-electron density of states. The substitution of B for Ga creates local crystal cell distortions of cubic phase due to the differences in the B and Ga atomic radii. These distortions may induce a shuffling of the atomic planes in the martensitic phase resulting in a 5 or 7 M modulated tetragonal structure. In [29] it has been found that such modulations will lower the energy of the martensitic phase, and therefore increase its stability.

In our present study we have assumed that the substituted B atom goes on the Ga position. This replacement of Ga by B decreases in the interatomic distance between Mn atoms. A theoretical study (see [28]) of the pressure dependence of T_C in Ni_2MnSn Heusler alloys shows that T_C changes with a change in interatomic exchange interaction. It has been shown that the T_C of Ni–Mn–Ga Heusler alloys depends on the Mn–Mn average distance. The study shows that T_C increases with a decrease of Mn–Mn distance and reaches a maximum value for a certain Mn–Mn distance (see [28]). For a further decrease of the Mn–Mn distance T_C starts to decrease. It has also been found that the increase of the magnetic moment of the alloy may or may not increase T_C [30]. Our study along with previous results of the isoelectronic substitution of Ga in Ni_2MnGa shows that T_C decreases for an increase or decrease of Mn–Mn distance. So the decrease of T_C for $Ni_2Mn(GaX)$ (where X is an isoelectronic atom with respect to Ga) can be explained based on RKKY interaction. The RKKY-type interaction is of oscillatory type in nature, changing both the magnitude and sign depending on the Mn–Mn distance. The decrease in the Mn–Mn distance in $Ni_2Mn(GaB)$ alloys could result in weakening of the exchange interaction and, therefore, a decrease in T_C.

In conclusion, we have shown that a single phase, quasi-ternary solid solution of $Ni_2MnGa_{1-x}B_x$ exists for boron concentrations $x \leqslant 0.01$. The substitution of B for Ga decreases the crystal cell parameter of the cubic phase. The decrease in cell parameter is due to the decrease of the cell volume resulting from substitution of a smaller atom (B atom) instead of a larger atom (Ga atom). The saturation magnetization at 5 K decreases with increasing B concentration. The decrease of M_S is most likely due to the oscillatory character of the Mn–Mn exchange interaction. The martensitic transition temperature increases rapidly with increase of B concentration. The observed change of T_M for $x \leqslant 0.1$ may be an effect of the crystal cell distortion and reduction of crystal cell volume. The Curie temperature was found to decrease slightly with increasing boron concentration for the low concentration interval. The decrease of T_C is attributed to weakening of the exchange interaction.

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