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## The role of Ni-Mn hybridization on the martensitic phase transitions in Mn-rich Heusler alloys

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Room temperature x-ray diffraction, dc magnetization, and ac susceptibility measurements have been performed on a series of Mn rich  $\text{Ni}_{50}\text{Mn}_{37-x}\text{Cr}_x\text{Sb}_{13}$  and  $\text{Ni}_{50+x}\text{Mn}_{37-x}\text{Sb}_{13}$  Heusler alloys. Depending on the value of  $x$ , the room temperature crystal structures of the samples are either  $L2_1$  cubic or orthorhombic. It is a commonly accepted idea that the martensitic transition temperatures in Ni-Mn-Z (Z = Ga, In, Sb, Sn) based Heusler alloys decrease (increase) with decreasing (increasing) valence electron concentration,  $e/a$ . However, the present work shows that regardless of the change in  $e/a$ , the martensitic transition temperature ( $T_M$ ) decreases with increasing Cr or Ni concentration. These results support the model where, in the case of Mn rich Heusler alloys, it is the hybridization between the Ni atoms and the Mn atoms in the Z sites that plays the dominant role in driving the martensitic transformation. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4705422>]

The Mn rich  $\text{Ni}_{50}\text{Mn}_{50-x}\text{Z}_x$  (Z = In, Sb, Sn) based Heusler alloys have gained significant interest in recent years due to their rich fundamental physics and potential as multifunctional materials.<sup>1-5</sup> The multifunctional properties of these alloys include large magnetocaloric effects,<sup>2,6,7</sup> giant magnetoresistance,<sup>8</sup> magnetic shape memory effects,<sup>9</sup> barocaloric effects,<sup>10</sup> and exchange bias effects.<sup>11,12</sup> Most of these exciting properties are associated with the coupled magneto-crystalline martensitic phase transition during which the high temperature cubic  $L2_1$  phase (austenite) of the alloys transforms to a low temperature phase (martensite) with a lower symmetry. The structure of the martensite is composition dependent and may be orthorhombic or monoclinic.<sup>1,3,13</sup> Both antiferromagnetic and ferromagnetic correlations play important roles in the magnetism of the martensitic phase, whereas the austenite exhibits ferromagnetic correlations.<sup>14</sup>

In  $\text{Ni}_{50}\text{Mn}_{50-x}\text{Z}_x$  alloys, the martensitic transition temperature,  $T_M$ , is generally believed to be dependent on the valence electron concentration,  $e/a$ .  $T_M$  generally increases (decreases) with increasing (decreasing)  $e/a$ .<sup>13</sup> However, in recent literature a few observations have been reported where  $T_M$  was found to depend non-monotonically on  $e/a$ . For example, when Mn is replaced by Cu in  $\text{Ni}_{50}\text{Mn}_{35-x}\text{Cu}_x\text{Sn}_{15}$ ,  $T_M$  first increases and then decreases rapidly with increasing Cu concentration (increasing  $e/a$ ).<sup>15</sup> In the case where Mn is replaced by Fe in  $\text{Ni}_{50}\text{Mn}_{38-x}\text{Fe}_x\text{Sb}_{12}$  and  $\text{Ni}_{50}\text{Mn}_{36-x}\text{Fe}_x\text{Sn}_{14}$ , a monotonic decrease of  $T_M$  with increasing  $e/a$  is observed.<sup>16,17</sup> These observations, along with several others,<sup>18</sup> suggest that, regardless of the  $e/a$  concentration,  $T_M$  decreases and eventually disappears when Ni or Mn is partially replaced by another transition metal in the  $\text{Ni}_{50}\text{Mn}_{50-x}\text{Z}_x$  alloys.

Ye *et al.* recently investigated the temperature dependence of the electronic structures of  $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$  by means of bulk-sensitive, hard-x-ray photoelectron spectroscopy and *ab initio* calculations.<sup>19</sup> According to this study, the Ni-Mn

hybridization is the main driving force for the martensitic transformation in Mn-rich Ni-Mn-Z alloys. In this case, once the hybridization is established, any change in the Ni or Mn concentration will weaken the hybridization, leading to the disappearance of the martensitic transformation and stabilization of the  $L2_1$  structure. This implies that  $e/a$  will have a minimal role (if any) on the stabilization of the martensitic phase.

Although a few studies (as mentioned above) indicate that this is the case, in order to confirm that Ni-Mn hybridization is the main factor that determines the stabilization of the martensitic phases rather than  $e/a$ , a more systematic study is needed, where  $e/a$  is varied in the same parent compound. Therefore, we have performed a systematic experimental study on a series of  $\text{Ni}_{50}\text{Mn}_{37-x}\text{Cr}_x\text{Sb}_{13}$  and  $\text{Ni}_{50+x}\text{Mn}_{37-x}\text{Sb}_{13}$  alloys by using dc magnetization and ac susceptibility measurements. The strategy was to observe the change in  $T_M$  with increasing and decreasing  $e/a$  while using the same ( $\text{Ni}_{50}\text{Mn}_{37}\text{Sb}_{13}$ ) parent compound in both alloy systems. In the case of  $\text{Ni}_{50}\text{Mn}_{37-x}\text{Cr}_x\text{Sb}_{13}$ ,  $e/a$  decreases with increasing Cr concentration, while  $e/a$  increases with increasing Ni concentration in  $\text{Ni}_{50+x}\text{Mn}_{37-x}\text{Sb}_{13}$  alloys. In both cases, the Mn content was reduced in a similar fashion. This strategy allowed us to observe the change in  $T_M$  as a function of both Mn content and  $e/a$ .

The Ni, Mn, Cr, and Sb metals used in preparing the alloys were obtained from Alfa Aesar Inc. and were of 4N purity. Approximately 2 g polycrystalline buttons of each alloy were prepared by conventional arc-melting in an argon atmosphere. The weight loss after melting was found to be less than 0.3%. For homogenization, the samples were annealed in vacuum for 72 h at 850 °C, followed by quenching in cold water. The  $e/a$  was calculated from the chemical formula of the compound; it is equal to the concentration weighted sum of the number of 3d and 4s electrons of Ni

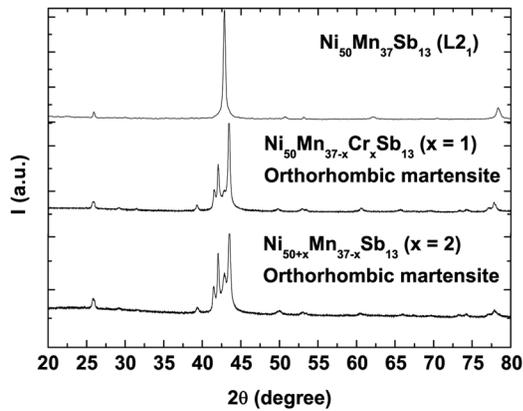


FIG. 1. Room temperature XRD patterns of selected alloys.

( $3d^84s^2$ ), Mn ( $3d^54s^2$ ), and Cr ( $3d^54s^1$ ) and the number of 5s and 5p electrons of Sb ( $5s^25p^3$ ).<sup>1,18,20</sup> The structural properties of the alloys have been checked by performing room temperature x-ray powder diffraction (XRD) on a Rigaku diffractometer employing monochromatic Cu  $K\alpha_1$  radiation. The crystal structure and the lattice parameters were determined by performing Reitveld refinement using LHPM-RIETICA.<sup>21</sup> The ac susceptibility measurements were conducted in a homemade ac susceptibility setup in zero dc magnetic field. The magnetization measurements were performed in a superconducting quantum interference device SQUID manufactured by Quantum Design, Inc. The measurements were performed in a temperature range of 10-400 K and in a magnetic field of 100 Oe.

Figure 1 shows illustrative room temperature XRD patterns for  $Ni_{50}Mn_{37}Sb_{13}$ ,  $Ni_{50}Mn_{37-x}Cr_xSb_{13}$  ( $x=2$ ), and  $Ni_{50+x}Mn_{37-x}Sb_{13}$  ( $x=1$ ). The parent alloy ( $Ni_{50}Mn_{37}Sb_{13}$ ) exhibits the cubic  $L2_1$  structure at room temperature. As Mn is partially replaced by either Cr or Ni, the  $L2_1$  structure

transforms to the 4O modulated orthorhombic structure.<sup>22</sup> As  $x$  exceeds 2, the  $L2_1$  cubic structure is restored and preserved for alloys with larger values of  $x$ .

Figure 2 shows the magnetization as a function of increasing temperature,  $M(T)$ , of the  $Ni_{50}Mn_{37-x}Cr_xSb_{13}$  alloys measured at a magnetic field of 100 Oe. Before the zero-field-cooled (ZFC) measurement, the sample was cooled down from room temperature to 10 K in zero magnetic field. In case of the field-cooled heating (FCH) measurement, the sample was cooled to 10 K in the presence of a 100 Oe magnetic field. The ZFC  $M(T)$  data of the alloy with  $x=0$  exhibit three transitions (see Fig. 2(a)) that are typically observed in these alloys.<sup>4,5</sup> The exchange bias blocking temperature,  $T_{EB}$ , was observed at 74 K followed by  $T_M$  at 293 K, and the ferromagnetic transition temperature of the austenitic phase,  $T_C^A$  at 342 K. As usual, due to pinning effects,  $T_{EB}$ , was only observed in the ZFC  $M(T)$  data. As Mn is initially replaced by a small amount of Cr ( $x=1$ ), an additional transition (ferromagnetic transition temperature,  $T_C^M$ , of the martensitic phase) is observed in the alloy, while  $T_M$  shifted to higher temperature. It is interesting to note that the transition at  $T_C^M$ , and the increase of  $T_M$ , were only observed in the alloys with  $x=1$  and 2. With a further increase of Cr concentration,  $T_M$  decreases rapidly and disappears as  $x$  exceeds 5. As shown in the ac susceptibility data in Fig. 3, similar behavior was observed when Mn was partially replaced with Ni in  $Ni_{50+x}Mn_{37-x}Sb_{13}$ .  $T_C^M$  is only observed in the alloys with  $x=1$  and 2, while  $T_M$  initially increases with increasing Ni concentration, and then decreases rapidly upon further increase of Ni. Since we are primarily interested in the transition temperatures  $T_M$ ,  $T_C^M$ , and  $T_C^A$ , only ac susceptibility measurements were conducted on the  $Ni_{50+x}Mn_{37-x}Sb_{13}$  samples.

In Fig. 4 the transition temperatures,  $T_M$ ,  $T_C^M$ , and  $T_C^A$  of the  $Ni_{50}Mn_{37-x}Cr_xSb_{13}$  and  $Ni_{50+x}Mn_{37-x}Sb_{13}$  alloys are

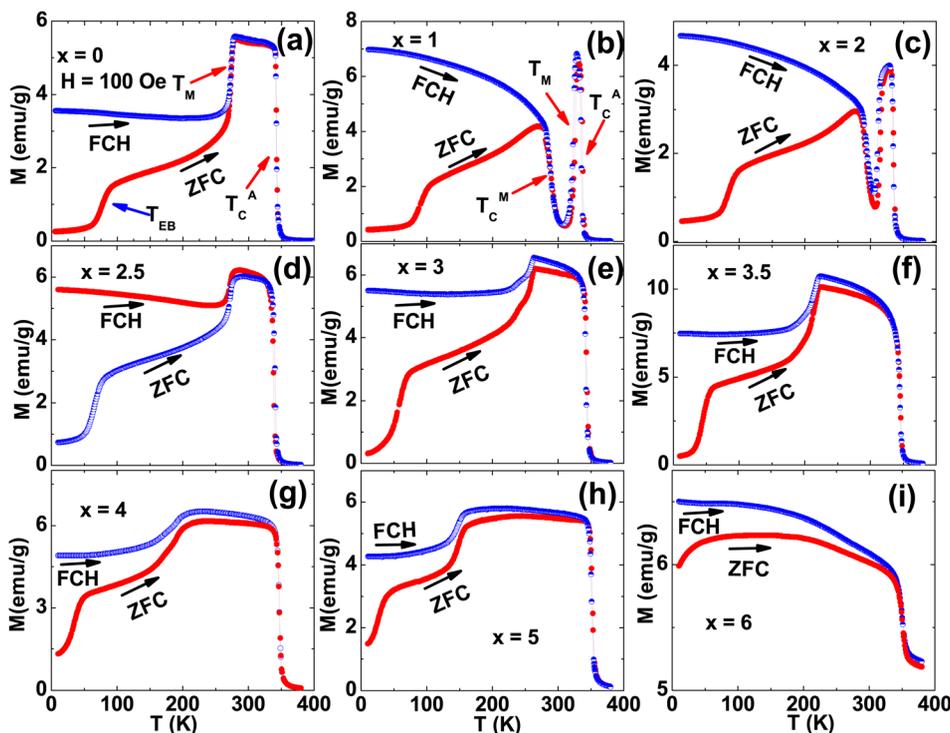


FIG. 2. Magnetization as a function of increasing temperature of  $Ni_{50}Mn_{37-x}Cr_xSb_{13}$  alloys measured at a magnetic field of 100 Oe.

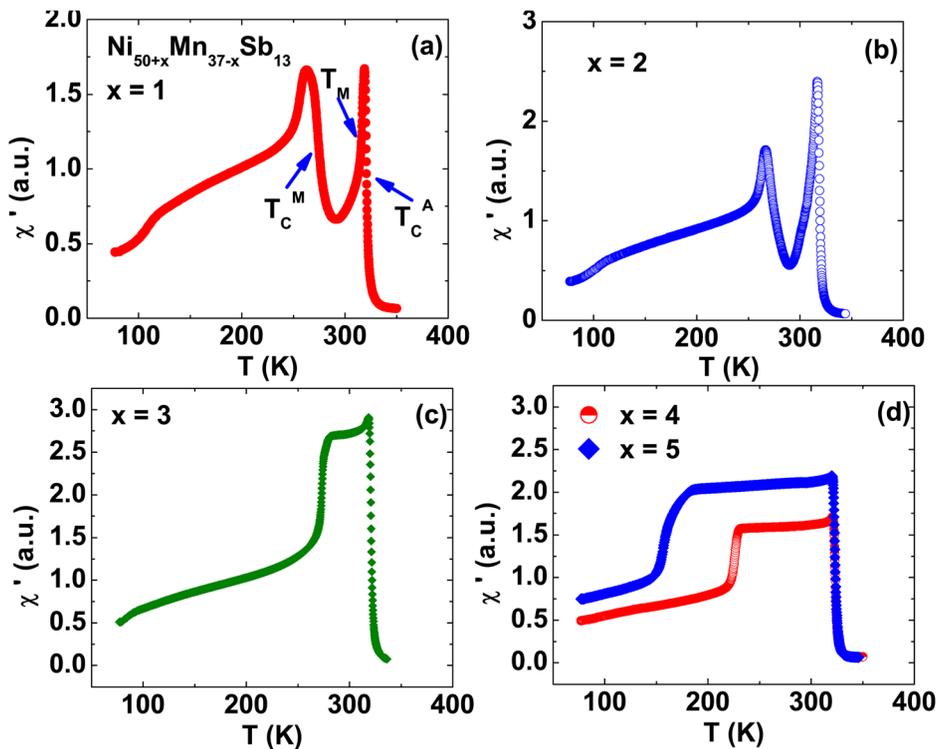


FIG. 3. The real component of the ac susceptibility of  $\text{Ni}_{50+x}\text{Mn}_{37-x}\text{Sb}_{13}$  alloys.

plotted as a function of  $e/a$ . As mentioned earlier, with increasing Cr concentration,  $e/a$  decreases in the  $\text{Ni}_{50}\text{Mn}_{37-x}\text{Cr}_x\text{Sb}_{13}$  system, while  $e/a$  increases with increasing Ni concentration in  $\text{Ni}_{50+x}\text{Mn}_{37-x}\text{Sb}_{13}$ . For each system,  $T_C^M$  was observed only in two alloys, and hence a proper discussion of their dependence on  $e/a$  cannot be made.  $T_C^A$  shows a generally slowly decreasing trend with increasing  $e/a$ . This behavior is consistent with earlier observations where  $T_C^A$  slowly decreases with increasing  $e/a$ .<sup>5</sup> The most interesting behavior observed in Fig. 4 is the nature of the variation of  $T_M$  with  $e/a$ . It is clear that, regardless of the change in  $e/a$ ,  $T_M$  decreases with decreasing Mn concentration.

Ye *et al.*<sup>19</sup> investigated the correlation between the electronic structure and martensitic phase transition of  $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$  by hard x-ray photoelectron spectroscopy

and *ab initio* calculation. In their study, they discovered that a strong hybridization takes place between the Ni 3d  $e_g$  states and the 3d states of the excess Mn atoms at the Sn sites, which are antiferromagnetically coupled with the Mn on the regular site. This hybridization is believed to be the main reason causing the martensitic transition in  $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$ . The role of hybridization in driving the martensitic phase transition in Heusler alloys was also demonstrated by Roy *et al.*<sup>23</sup> who showed by various experimental means that partial replacement of Mn by Cu in  $\text{Ni}_2\text{Mn}_{0.75}\text{Cu}_{0.25}\text{Ga}$  enhanced the Ni-Ga hybridization resulting in a shift of  $T_M$  to higher temperature. In light of these studies, especially the observations by Ye *et al.*, we propose that the main driving force behind the martensitic transformation in Mn-rich Heusler alloys is the hybridization between the Ni 3d  $e_g$  states and the 3d states of the excess Mn atoms at the Sn sites. In such a scenario, once the hybridization is established, any change in the Ni or Mn content will tend to weaken the hybridization, and result in a decrease of  $T_M$ . This idea is strongly supported by the results shown in Fig. 4 as well as by the results reported earlier where, regardless of the change in  $e/a$ ,  $T_M$  in Mn-rich Ni-Mn-Z Heusler alloys decreases when Ni or Mn is partially replaced by a different element. Based on these observations, it can be concluded that the widely accepted idea that  $T_M$  monotonically follows  $e/a$  does not apply to Mn-rich Heusler alloys.

In summary, we have performed an experimental study on  $\text{Ni}_{50}\text{Mn}_{37-x}\text{Cr}_x\text{Sb}_{13}$  and  $\text{Ni}_{50+x}\text{Mn}_{37-x}\text{Sb}_{13}$  Heusler alloys. With increasing Cr concentration  $e/a$  decreases in  $\text{Ni}_{50}\text{Mn}_{37-x}\text{Cr}_x\text{Sb}_{13}$ , whereas  $e/a$  increases with increasing Ni concentration in  $\text{Ni}_{50+x}\text{Mn}_{37-x}\text{Sb}_{13}$ . Regardless of the change in  $e/a$ , in both cases  $T_M$  decreases with increasing Cr or Ni concentration, suggesting that the well developed idea of  $T_M$  monotonically following  $e/a$  does not apply to Mn-rich Heusler alloys. We suggest that the dominant factor,

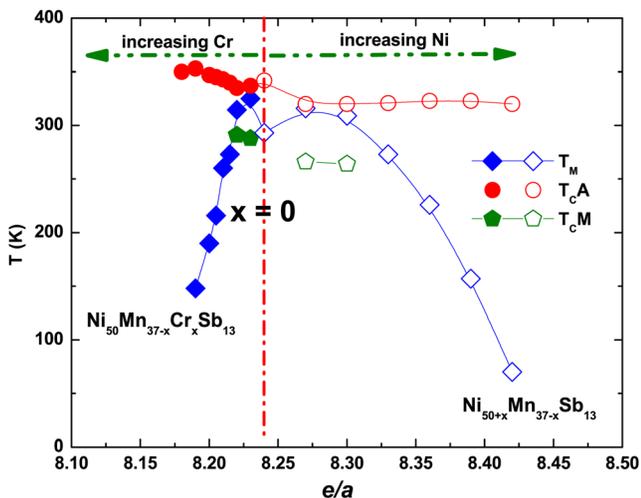


FIG. 4. The transition temperatures as a function of  $e/a$  of  $\text{Ni}_{50}\text{Mn}_{37-x}\text{Cr}_x\text{Sb}_{13}$  and  $\text{Ni}_{50+x}\text{Mn}_{37-x}\text{Sb}_{13}$  alloys.

which affects the behavior of the martensitic transition is the nature of hybridization between the Ni 3d  $e_g$  states and the 3d states of the excess Mn atoms at the Sn sites, which are antiferromagnetically coupled.

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<sup>20</sup>For example, the formula for calculating  $e/a$  for the parent compound,  $\text{Ni}_{50}\text{Mn}_{37}\text{Sb}_{13}$  is
- $$e/a = \frac{50 \times 10 + 37 \times 7 + 13 \times 5}{50 + 37 + 13} = 8.24 \quad (1)$$
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