Correlation of martensitic transformation temperatures of Ni-Mn-Ga/Al-X alloys to non-bonding electron concentration

M. Ramudu¹, A. Satish Kumar¹, V. Seshubai¹ and T. Rajasekharan²
School of physics, University of Hyderabad, Gachibowli, Hyderabad-500 046, India.
Rajiv Gandhi University of Knowledge Technologies, Vindhya C4 building, IIIT-Campus, Hyderabad - 500 032, India.
macrams2@gmail.com

Abstract. The martensitic transformation $T_M$ of the alloys of Ni-Mn-Ga and Ni-Mn-Al show a general trend of increase with electron per atom ratio ($e/a$) calculated from the total number of electrons outside the rare gas shell of the atoms. However prediction of $T_M$ fails among iron substituted Ni-Mn-Ga alloys and those with In doped for Ga, due to the absence of a useful trend. A scheme of computing modified electron concentration is presented considering only the non-bonding electrons per atom $N_{e/a}$ of the compounds, based on Pauling’s ideas on the electronic structure of metallic elements. Systematic variation of $T_M$ with $N_{e/a}$ is reproduced for a large number of alloys of Ni-Mn-Ga and the anomaly observed for Fe containing alloys with $e/a$ disappears. The non-bonding electron concentration is thus demonstrated to be effective in predicting $T_M$ of shape memory alloys of Ni-Mn-Ga-X system including the isoelectronic compounds of Ni-Mn-Ga-In.

1. Introduction
The study of magnetic shape memory alloys has, of recent, gained momentum due to their potential for applications as sensors and actuators operable at room temperature [1]. Also, their application in magnetic refrigeration is much sought after due to the benefits that could ensue to the environment [2]. Off-stoichiometric compositions derived from ferromagnetic Ni$_2$MnGa Heusler alloy, are widely studied in this context. The magnitude of magnetic field induced strain in these alloys is governed by key factors like martensitic transformation temperature ($T_M$), Curie temperature ($T_C$), saturation magnetization, magnetocrystalline anisotropy and the nature of twin deformation in martensitic phase. Various elements have been substituted to fine tune $T_M$ and the modifications caused to the microstructures and physical properties, is investigated. There are several reports on systematic dependence of $T_M$ on the electron per atom ratio $e/a$, in these alloys. Here, $e/a$ is computed as an average of the number of electrons beyond the rare gas shell of the atoms constituting the alloy. Systematic dependence of $T_M$ on the electron per atom ratio ($e/a$) is reported in Ni-Mn-X ($X = $ Ga, Al, Sn, In and Sb) alloys. However, iron substituted Ni-Mn-Ga alloys have been observed to be anomalous in their behavior; and their deviation from the normal trend has been discussed in several publications [3-5]. Also in the case of isoelectronic substitutions like In- substituted for Ga, where $e/a$ remains unaltered, prediction of $T_M$ fails. We discuss in this paper, an alternative scheme of computing effective valence electrons per atom, $N_{e/a}$. We examine the trend of variation in $T_M$ with $N_{e/a}$ for a number of shape memory alloys of Ni-Mn-Ga system and discuss its efficacy in predicting $T_M$ for isoelectronic and iron substituted alloys as well.
2. Present model, an extension of Pauling’s approach
In this approach, Pauling’s idea of transfer of charge \([6, 7]\) on an atom-pair bond to maintain electroneutrality in metallic alloys is adopted. In this model \([7-9]\), Miedema’s parameters \(\Theta\) and \(N_{\alpha}\) were considered to represent the electronegativity and valence of metallic elements respectively. These parameters were defined by Miedema as work function and the ‘electron density at the boundary of the Wigner-Seitz cells’ of the elements and were used by him to compute semi-empirically, the heats of formation \((\Delta H)\) of binary alloys \([10]\). This model is shown to accurately predict concomitant and mutually exclusive crystal structure types in metallic binary systems \([8]\). The versatility of the above approach suggests that Pauling’s scheme of filling electrons in orbitals of metallic atoms could be of interest in predicting the magnetic and electrical properties of metallic alloys. Pauling’s approach provided a qualitative explanation \([11, 12]\) of many properties of the transition metals such as interatomic distance, hardness, compressibility, and coefficient of thermal expansion, and it accounts satisfactorily for the observed values of the atomic saturation magnetic moments of the ferromagnetic elements iron, cobalt, and nickel and their alloys.

Pauling had proposed \([11]\) that in metals, d-orbitals alone are not especially well suited to use in bond formation, but hybridization of d, s, and p orbitals leads to the best bond orbitals known. There are available a total of nine relatively stable orbitals: five 3d, one 4s, and three 4p for the iron group elements, and corresponding sets for other series. If \(N_p\) is the Pauling’s valence of an element, \(N_p\) electrons would fill up unpaired in the bond orbitals and would be available for the formation of \(N_p\) electron-pair bonds with other atoms. Melting and boiling points of elements would therefore be proportional to \(N_p\).

Let \(O\) be the total number of orbitals of an atom; Pauling had argued that \(O = 9\), consisting of five 3d, one 4s, and three 4p orbitals for the iron group elements, and corresponding sets for other series \([11]\). Let \(E\) be the total number of electrons beyond the inert gas shell of an atom and \(N_{\alpha}\) be the valence of a metal; Pauling had proposed that \(N_{\alpha}\) orbitals would be filled by an equal number of unpaired electrons which would form resonating covalent bonds with the neighboring atoms. The number of electrons not involved in bonding would be \(E - N_{\alpha}\). Such electrons were referred to as paired non-bonding electrons by Pauling. In the modified Pauling’s scheme, we have used Miedema’s corrected electron density parameter \(N_{\alpha}\) as the valence of metals. The choice of Miedema’s electron density parameter \(N_{\alpha}\) as the valence of metallic elements (instead of \(N_{\alpha}\)) is discussed in detail elsewhere \([7]\). Then, \(N_{\alpha}\) electrons per atom would occupy \(N_{\alpha}\) orbitals, i.e., one electron per orbital, and form covalent bonds with the neighboring atoms. The residual electrons fill the remaining 9-\(N_{\alpha}\) orbitals in pairs. These electrons are nonbonding electrons and they contribute to magnetism, electrical properties etc. In the case of ferromagnetic elements such as Fe, Co and Ni, a certain number of the nonbonding electrons would remain unpaired, contributing to the magnetic moments of the atoms. The number of non-bonding electrons is calculated as \((E-N_{\alpha})\), where \(E\) is the number of electrons beyond the rare gas shell of the atom.

In the following, we consider the non-bonding electrons \((e_{\alpha})\) to represent the number of electrons per atom relevant in dictating the physical properties of metallic alloys. We compute the effective ‘non-bonding electrons per atom’ of a compound \((N_{\alpha})\) from a knowledge of \(e_{\alpha}\) contributed by each atom. The values of \(N_{\alpha}\) for the elements Ni, Mn, Ga, Co, Fe, Al, and In are 5.36, 4.17, 2.25, 5.36, 5.55, 2.69, and 1.6, respectively \([10]\). As a typical example demonstrating how \(N_{\alpha}\) for an alloy is calculated, we consider the calculation for Ni\(_{50}\)Mn\(_{30}\)Ga\(_{20}\). The values of \((E, N_{\alpha}\) and \(e_{\alpha}\) for Ni, Mn and Ga are \((10, 5.36\) and 4.74), \((7, 4.17\) and 2.83) and \((3, 2.25\) and 0.75), respectively. \(N_{\alpha}\) for the compound can be computed as \(\{50 \times (10-5.36) + 26 \times (7-4.17) + 24 \times (3-2.25)\}/100 = 3.24\).

3. Systematics in the dependence of \(T_M\) on electron concentration
The martensitic transformation temperatures \(T_M\) of 171 off-stoichiometric alloys in the Ni-Mn-Ga system, 84 quasi-ternary alloys with Co substitution, 76 alloys with Fe substitution, and 7 alloys with indium substitution in Ni-Mn-Ga system, were collected from compilations \([1, 2]\) and individual reports in the literature \([3, 4, 13, 14, 15-18, 19-32]\). The \(e/a\) values of the compounds were computed taking the \(E\) values to represent the valences of Ni, Mn, Ga, Co, Fe and In which are 10, 7, 3, 9, 8, 3
and 3 respectively; the individual electron contributions of all atoms are added up in the formula unit and divided by the total number of atoms [33].

The variations in the martensitic transformation temperatures of off-stoichiometric alloys and Co-doped alloys of Ni$_2$MnGa with $e/a$ and $N_{\text{e/a}}$ are given in figure 1. Figure 1 shows that the correlations of $T_M$ with $e/a$ and $N_{\text{e/a}}$ are equally good for the above alloys. Figure 1 (a) and (b) for off-stoichiometric Ni$_2$MnGa, shows three regions. 141 alloys out of a total of 171 alloys with $e/a \leq 7.72$ show a linear variation of $T_M$ with $e/a$. The compounds with $e/a > 7.72$ are the Ni-rich ones having $T_M > T_C$, with potential for high temperature shape memory applications. Most of these compounds, which have non-modulated tetragonal structure, show a faster increase in $T_M$ with $e/a$. This has been attributed to a decrease in their unit cell volumes due to smaller Ni atoms replacing the larger Ga atoms in the crystal lattice. A combination of increase in $e/a$ and a decrease in cell volumes causes a faster increase in effective electron concentration and hence in the $T_M$ of those alloys [22]. At Ni contents in excess of 57 at.%, $\gamma$-phase precipitates out and the concentration of the alloy remains a constant, leading to a constant $T_M$ for $e/a$ values greater than 8.0 (see figure). The $e/a$ values were computed from the nominal composition of the alloys. Figures 1 (c) and (d), show a linear trend of $T_M$ with $e/a$ as well as $N_{\text{e/a}}$ for Co-doped Ni-Mn-Ga alloys.

On the contrary, we note from figure 2(a), that the variation of $T_M$ with $e/a$ for Fe-doped compounds of Ni-Mn-Ga distributed at random. The anomalous behavior of iron-containing alloys has been discussed by several authors [3-5]. It has been attributed to factors other than $e/a$ also contributing to the stability of those phases, like the site occupied in ordered structure [29], volume effects associated with atomic sizes [5, 31], magnetic contributions [3] etc. We now examine the variation of $T_M$ with the non-bonding electrons per atom, $N_{\text{e/a}}$ in figure 2 (b) for the iron-substituted alloys of Ni$_2$MnGa. The regression factor (R) shows a remarkable improvement from R = 0.175 for $T_M$ with $e/a$ to R = 0.80 for the plot of $T_M$ with $N_{\text{e/a}}$. Hence the correlation of $T_M$ with $N_{\text{e/a}}$ can be used to predict $T_M$ of new compositions in the Ni-Mn-Ga-Fe system. The anomalous behavior seen in Fe-containing compounds when using the earlier electron counting scheme (using $e/a$) is thus resolved.

We consider below the case of isoelectronic substitutions like Ni$_2$MnGa$_{1-x}$In$_x$ alloys. In figure 3 (a) we observe that the $T_M$ versus $e/a$ plot for Ni$_2$MnGa$_{1-x}$In$_x$ alloys does not exhibit any useful trend since the valences assumed conventionally are the same for the isoelectronic elements like Ga.
and In, viz. 3. In figure 3 (b) we show the dependence of $T_M$ on the non-bonding electrons per atom ($N_{e/a}$) which shows a systematic variation, but a decreasing trend rather than an increasing trend of $T_M$ with $N_{e/a}$ as observed in other compounds. We examine below the possible role of volume effects discussed in literature [34], associated with large difference in the atomic sizes of Ga and In. We computed $N_{e/V}$ that defines the electron concentration per unit volume. Here, V is calculated as the average (atomic) volume per atom. Figure 3 (c) shows that the trend of variation in $T_M$ with $N_{e/a}$ reverses with $N_{e/V}$ for Ni$_2$MnGa$_{1-x}$In$_x$ alloys confirming the role of volume effects. The various results discussed above suggest that computing non-bonding electron concentration is worth exploring to understand the mechanisms determining the martensitic transformation temperatures in shape memory alloys.

4. Conclusions

Significance of computing the non-bonding electron concentration ($N_{e/a}$) to predict the martensitic transformation temperatures of $T_M$ of shape memory alloys of Ni-Mn-Ga system is demonstrated. A plot of $T_M$ with $N_{e/a}$ shows a systematic variation for alloys derived from Ni-Mn-Ga and resolves the anomaly observed for Fe containing alloys with $e/a$.

Acknowledgements: MR acknowledges UGC-RFSMS for financial support in the form of fellowship. ASK and VS thank CSIR, India, for research funding (03(1065) 106/EMR-II).

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