Ferromagnetic/Antiferromagnetic Exchange Coupling in Ni$_2$MnSn-derived Magnetic Shape Memory Alloys

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Abstract. The magnetic behaviour of Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ ferromagnetic (FM) shape memory alloys are investigated with a focus on the exchange coupling and the ground state magnetic properties. Large exchange bias in the field cooled state of $x = 0.36, 0.44$ alloys is observed, which strongly varies with the cooling field. The observed exchange coupling was found to originate right from a characteristics step like anomaly in the zero-field-cooled magnetization versus temperature data. The step like anomaly shows clear frequency shift in the ac susceptibility data, indicating the development of spin frustration arising from the incipient antiferromagnetic (AFM) correlations in the otherwise FM alloy. Interestingly, the zero field cooled magnetic hysteresis loops in the studied samples show constricted double loop structure, which on field cooling shifts asymmetrically depending upon the sign of the cooling field. This indicates the complex AFM domain structure originating from the FM/AFM coupling.

1. Introduction

The shape and size of the ferromagnetic magnetic hysteresis loop can be related to various intrinsic as well as extrinsic parameters. For a heterogeneous magnetic system, the interfacial spin-spin coupling can play important role in determining the nature of the magnetization loop. The classic example is the observation of exchange bias (EB), where exchange pinning at the ferromagnetic (FM)/anti-ferromagnetic (AFM) interface can cause a shift in the hysteresis loop in field-cooled state [1]. Recently, EB has been observed in case of various Ni-Mn-Z (Z = Sn, In, Sb) based Heusler type ferromagnetic shape memory alloys (FSMAs) [2, 3, 4]. Magnetic studies including EB and theoretical analysis indicates the coexistence of FM and AFM phases in Ni-Mn-Z alloys, particularly below the martensitic transition (MT) [5]. In the present work, we report the detailed magnetic investigations on polycrystalline Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ ($x = 0.36, 0.44$) FSMAs [6], which show EB phenomenon. The present samples were prepared by argon arc melting and subsequent annealing at 900 °C. The compositions of the samples, checked by Energy dispersive spectroscopy (EDS), were found to be close to the nominal values within the accuracy of the method.

2. Results and Discussions

The magnetic measurements were performed both on Quantum Design SQUID magnetometer as well as on a vibrating sample magnetometer (with ac susceptibility option) from Cryogenic Ltd. UK. Fig. 1 (a) and (b) show the magnetization ($M$) vs. temperature ($T$) data for $x =$
Figure 1. (a) and (b) show thermal variation of magnetization for Ni$_{2}$Mn$_{1+x}$Sn$_{1-x}$ ($x = 0.36$ and 0.44) alloys respectively. (c) and (d) depict isothermal magnetization as a function of field at 5 K in ZFC and FC (cooled in 0.5 and 2.5 kOe from 300 K) states for $x = 0.36$ and 0.44 respectively. (e) and (f) depict exchange field ($H^E$) and shift in magnetization ($M^E$) as a function of cooling field ($H_{cool}$) for Ni$_{2}$Mn$_{1+x}$Sn$_{1-x}$ ($x = 0.36$ and 0.44) alloys.

0.36 and 0.44 samples respectively. The onset of the MT (here we call it $T_M$) of the samples is evident from the deviation point between the ZFC (zero-field-cooled) and FC (field-cooled) heating data. Both the samples show a step like anomaly well below the MT, which has been denoted by $T_S$ in the figure. This step like anomaly is only observed in the ZFCH data and it is completely absent in the FCH measurement. In previous works on various Ni-Mn-Z FSMAs, similar step like anomaly was observed, and a close connection between the anomaly and the EB has become evident [2, 3, 4]. The EB was found to vanish above $T_S$, and it was considered as the EB blocking temperature.

The isothermal $M$ versus magnetic field ($H$) behaviour of the studied alloys recorded at 5 K are shown in fig.1(c) and (d) with different measurement protocols. For both the samples, there is a clear difference between the hysteresis loops when recorded in the FC and ZFC states. The FC hysteresis loops (cooled in $H = 0.5$ and 2.5 kOe) are found to be shifted both in the $H$ and $M$ axes as compared to the symmetric (with centres at the origin) ZFC loop. This is the indication of EB for the sample. The $M - H$ isotherms presented in fig.1 (c) and (d) were recorded between $\pm 20$ kOe, although only a enlarged view (between $\pm 2.5$ kOe) is shown here. $M - H$ cycling between $\pm 20$ kOe rules out the minor loop effect toward the observed EB, as the saturation fields for the present samples are much lower than 20 kOe.

The EB is generally expressed by the quantities $H^E$ and $M^E$, which are the shift of the FC hysteresis loop in the horizontal $H$ and vertical $M$ axes respectively. The variation of $H^E$ and $M^E$ with the cooling field ($H_{cool}$, the field under which sample is cooled down to 5 K) are depicted in fig. 1 (e) and (f). For both the samples, the variation is non-monotonous, the $H^E$ rises with the initial increase of $H_{cool}$, goes through a maximum (approximately for 0.5 kOe for both the samples), dropped for further increase of $H_{cool}$ and then shows a sluggish decrease with further increase of $H_{cool}$. Initially (before the saturation of FM fraction), increasing $H_{cool}$
enhances the EB by favouring the alignment of the FM fraction. However, for very high value of $H_{\text{cool}}$, it can reduce the interface by increasing the size of the FM clusters, and thereby reducing the EB.

The EB discussed so far were all recorded by cooling the sample from $T_{\text{max}} = 300$ K, which is well above the $T_M$ of both the materials. We also recorded isothermal loops (not shown here) by cooling the sample from different values of $T_{\text{max}}$. It is observed that $H_E$ for a particular cooling field remains almost same as long as $T_{\text{max}}$ is higher than $T_S$, the temperature where step like anomaly is observed in ZFCH $M-T$ data. However, if the samples are field cooled from a temperature which lies below $T_S$, no EB is seen [7]. This is true for both the alloys, although the value of $T_S$ is quite different for $x = 0.36$ and $x = 0.44$ samples. This signifies that $T_S$ actually represent the onset for the non-FM phase, which is responsible for interfacial coupling of the FM spins.

We also measured ac susceptibility on both the alloys around the step-like anomaly. Both real and imaginary parts of the ac susceptibility ($\chi_{ac}'$ and $\chi_{ac}''$ respectively) are shown in fig. 2 for $x = 0.36$ and $x = 0.44$ samples. Clear peak is observed in $\chi_{ac}''(T)$ data with peak position nearly matching with $T_S$ of the respective samples, and a clear shift in the peak temperature is observed with the change in frequency of the ac measurement. The peak temperature increases with the increasing frequency, which indicates that the peaks in both the samples are associated with the onset of spin freezing [8]. This is not unusual, considering the fact that the samples contain both FM and AFM components, which can give rise to a spin-glass (SG) type ground state. The AFM phase actually develops below the MT, however, only below $T_S$ the interfacial FM/AFM coupling becomes strong enough for the EB. The system also simultaneously show SG behaviour arising from the spin frustration at the interface.

Interestingly, around the origins, the ZFC $M-H$ hysteresis loops show a weak signature of constriction (indicated by arrows in fig.4). In other words, the loops are relatively narrower near the origin and then bulge out for both positive and negative fields. This is a typical double loop behaviour observed in various thin film multilayers containing both hard and soft magnetic materials [9]. Notably, similar constricted loops are also present in various Ni-Mn-Z-
Figure 3. Isothermal magnetization ($M$) data as a function of magnetic field ($H$) recorded at 5 K for $x = 0.44$ alloy. (a) and (b) show magnetization loops after being field cooled in 500 and -500 Oe respectively. Zero-field-cooled loop is also shown in both the plots for comparison.

type FSMAs [2, 4].

In fig. 3, we show $M - H$ loop for the $x = 0.44$ sample after being field cooled in 500 and -500 Oe of fields. Clear signature of EB is visible, with the loops being shifted to left (right) side along the field axis. It is evident that the two sub-loops (in the positive and negative quadrants respectively) of the double loop respond differently depending upon the sign of $H_{cool}$. If cooled in positive field, the shift is observed for the sub-loop in the positive quadrant only, while for negative $H_{cool}$, only the negative sub-loop shifts. A closer look at the hysteresis loop also brings out the fact that the region of constriction actually shifts from origin to finite value of $H$, which is close to $H_{cool}$ in magnitude as well as in sign.

For a bulk polycrystalline sample, with multiple grain and grain boundaries, it is difficult to ascertain the true cause of the double loop behaviour. But the behaviour, particularly depicted in fig. 3 is very similar to the case of FM/AFM multilayer system reported by Brück et al [10]. In presence of magnetic anisotropy in the martensite phase, the possible origin may lie in the existence of antiparallel FM domains in the system, which is exchange coupled with the AFM phase. This in effect locally pin the interfacial AFM spins in two opposite orientations giving rise to double loop phenomenon.

In conclusion, we report the observation of EB in Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ ($x = 0.36$ and 0.44) alloys. Both the samples show interesting spin-glass behaviour close to the EB blocking temperature, and the EB is found to be closely connected to the spin frustration arising from FM/AFM interactions. The samples also show constricted magnetization loop, which indicates the existence of complex magnetic domain structure.

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