Pressure effects on magnetic properties and martensitic transformation of Ni–Mn–Sn magnetic shape memory alloys*

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The mechanism for the effects of pressure on the magnetic properties and the martensitic transformation of Ni–Mn–Sn shape memory alloys is revealed by first-principles calculations. It is found that the total energy difference between paramagnetic and ferromagnetic austenite states plays an important role in the magnetic transition of Ni–Mn–Sn under pressure. The pressure increases the relative stability of the martensite with respect to the austenite, leading to an increase of the martensitic transformation temperature. Moreover, the effects of pressure on the magnetic properties and the martensitic transformation are discussed based on the electronic structure.

Keywords: ferromagnetic shape memory alloys, magnetic properties, martensitic transformation, electronic band structure

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1. Introduction

Off-stoichiometric Ni–Mn–Sn ferromagnetic shape memory alloys have attracted much attention since the discovery of the magnetic field-induced reverse martensitic transformation.[1–5] The magnetization in the martensite phase of these alloys is significantly smaller than that in the austenite phase. The transformation from the high-temperature austenite phase to the low-tenperature martensite phase with greatly reduced magnetization in Ni–Mn–Sn alloys gives rise to a number of interesting effects, such as the inverse magnetocaloric effect,[6–9] giant strain due to field-induced reverse martensitic transformation,[10,11] and giant magnetoresistivity.[12,13] These make the Ni–Mn–Sn alloys good candidates for multifunctional applications. In these alloys, the magnetic properties and the martensitic transformation are very sensitive to the composition. Apart from the composition, external parameters such as the pressure strongly influence the magnetic properties and the martensitic transformation.[14–18] The magnetic properties of the Ni–Mn–Sn alloys are dependent on the Mn–Mn distance, and any change in the Mn–Mn distance results in a modified exchange interaction. The pressure can influence the Mn–Mn distance and then the magnetic properties. It has been reported that the magnetizations of both austenite and martensite phases decrease with increasing pressure.[14] Moreover, the previous studies showed that the application of pressure significantly shifts the martensitic transformation temperature to higher values.[14,16] This fact opens up possibilities for controlling the magnetic properties and the martensitic transformation by means of an applied pressure. However, up to now, the mechanism for the pressure effects on the magnetic properties and the martensitic transformation of off-stoichiometric Ni–Mn–Sn alloys is still unclear.

In this paper, we reveal the mechanism for the effects of pressure on the magnetic properties and the martensitic transformation of $Ni_2Mn_{1+x}Sn_{1-x}$ ($x = 0.5$) alloys from the electronic structure point of view by using the first-principles calculations. The results provide theoretical data and directions for developing high performance metamagnetic shape memory alloys in Ni–Mn-based Heusler alloy systems.

2. Calculational methods

First-principles calculations have been performed based on the density functional theory by using the CASTEP code.[19] The interaction between ions and electrons is described by the ultra-soft pseudopotential.[20] The spin-polarized generalized gradient approximation is used to describe the exchange correlation energy. The plane-wave cutoff energy is 400 eV, and a (8, 8, 8) Monkhorst–Pack grid is employed to sample the Brillouin zone. For the cubic $L2_1$ austen-

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ite of $Ni_2Mn_{1+x}Sn_{1-x}$ ($x = 0.5$), a 16-atom unit cell is built with appropriate Sn atoms replaced by Mn atoms. A pressure from 0 GPa to 4 GPa is chosen where the experimental information is available. Each structure is optimized under a fixed pressure. The tetragonal martensite is obtained by calculating the stability of the $L2_1$ austenite with respect to the volume-conserving tetragonal distortion as a function of pressure. Then, the total energies, magnetic moments, and electronic structures of both austenite and martensite phases under pressure are calculated.

3. Results and discussion

Figure 1 illustrates the variation of the total magnetic moment with pressure for the Ni–Mn–Sn austenite. It can be seen that the total magnetic moment decreases linearly with increasing pressure, which is in agreement with the experimental results.[14] A decrease of the total magnetic moment from $2.02\mu_B$ at ambient pressure to $1.99\mu_B$ at an applied pressure of 4 GPa is observed. For the Ni–Mn–Sn alloy, the magnetic moment is mainly confined to the Mn atoms. The calculated results show that the dependence of the Mn magnetic moment on pressure can be well represented by a linear function with a negative slope. Moreover, our calculations indicate that the pressure dependence of the magnetic moment of the martensite is similar to that of the austenite. The decreases of the total and the atomic magnetic moments are closely related to the decrease of the lattice constant and broadening of the energy bands under pressure.

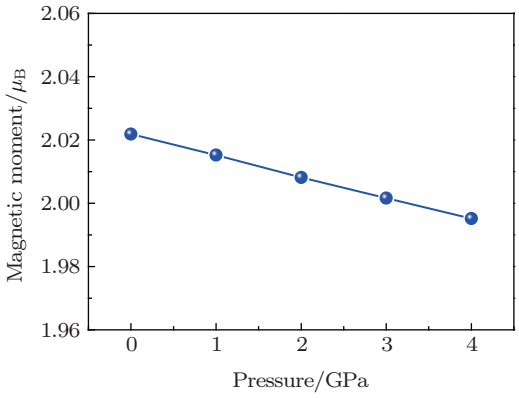


Fig. 1. (color online) Change of the total magnetic moment with the pressure in Ni–Mn–Sn austenite.

From the application point of view, the Curie temperature T_c is very important since it limits the operational temperature range of Ni–Mn–Sn based alloys. In order to investigate the effect of pressure on T_c, the total energies of both ferromagnetic and paramagnetic cubic austenite phases of the Ni–Mn–Sn alloys under different pressures are calculated. It is found that the total energy of the paramagnetic austenite is much higher than that of the ferromagnetic one with the compositions studied, which is consistent with the fact that the paramagnetic austenite is the high temperature phase. According to the Stoner theory, T_c can be taken to be proportional to the total energy difference between the paramagnetic and the ferromagnetic states.[21] Although this approximation gives a much higher value of T_c, it could be used to find the relative variation.[22] Figure 2 shows the total energy difference between paramagnetic and ferromagnetic states of the Ni–Mn–Sn austenite as a function of pressure. It is noted that the total energy difference decreases almost linearly with increasing pressure. This indicates that T_c of the Ni–Mn–Sn alloy decreases with increasing pressure, which is in fair agreement with the experimental observations.[15] However, the early work showed that T_c increases with increasing pressure for Ni_2MnSn.[23] The different pressure changes of T_c for the Ni–Mn–Sn alloys are related to the different pressure changes of the exchange interactions. As is well known, the exchange interactions in Mn-based alloys and compounds depend strongly on the Mn–Mn interactions. Recently, Şaşioğlu *et al.*[17] have studied theoretically the pressure dependence of the exchange interaction in Ni_2MnSn. Their analysis showed that the leading contribution to T_c is given by the exchange interaction J_{Mn-Mn} between the Mn atoms in the Mn sublattice, which increases monotonically with pressure increasing. While for the pressure effect of T_c in off-stoichiometric Ni–Mn–Sn alloys, it has been reported that the exchange interaction J'_{Mn-Mn} between the Mn atoms on the Mn sites (denoted as Mn_{Mn}) and on the Sn sites (denoted as Mn_{Sn}) is negative and competes with that of J_{Mn-Mn}. In terms of the competition between the two opposite trends, it can be suggested that the decrease of T_c in the off-stoichiometric Ni–Mn–Sn alloys under pressure is attributed to a stronger effect of J'_{Mn-Mn}.

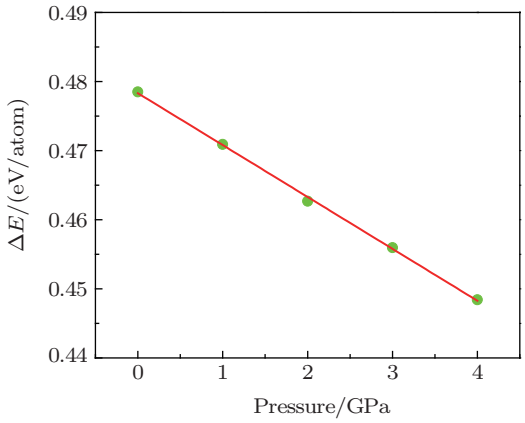


Fig. 2. (color online) Total energy difference between paramagnetic and ferromagnetic states of Ni–Mn–Sn austenite (ΔE) as a function of pressure.

The phase stability is critical to the properties of the martensitic transformation. Therefore, we investigate the pressure effect on the martensitic transformation of Ni–Mn–Sn in

terms of the relative stability of the martensite and austenite. Figure 3 shows the total energy of Ni–Mn–Sn as a function of c/a under various pressures, keeping the volume fixed at the equilibrium volume. The energy corresponding to the $L2_1$ austenite phase ($c/a = 1$) under each pressure is used as a reference. It can be seen that the minimum values, corresponding to the martensite, are located approximately at $c/a \sim 1.33$ for all pressures. In particular, it is found that increasing the pressure makes the martensite more stable than the austenite. Moreover, the stability of the martensite with respect to the austenite may be measured by the difference between their energies. It has been noted that a larger energy difference generally implicates a higher martensitic transformation temperature.[24] Figure 4 shows that the total energy difference between austenite and martensite of the Ni–Mn–Sn alloys as a function of pressure. It can be obviously seen that the total energy difference increases with increasing pressure. This suggests that the pressure increases the relative stability of the martensite with respect to the austenite, which is responsible for the increase of the martensitic transformation temperature.

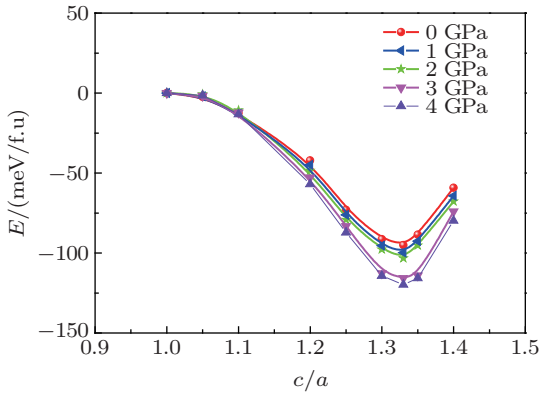


Fig. 3. (color online) Total energy of Ni–Mn–Sn as function of c/a under various pressures. The energy corresponding to the $L2_1$ austenite phase ($c/a = 1$) under each pressure is used as a reference.

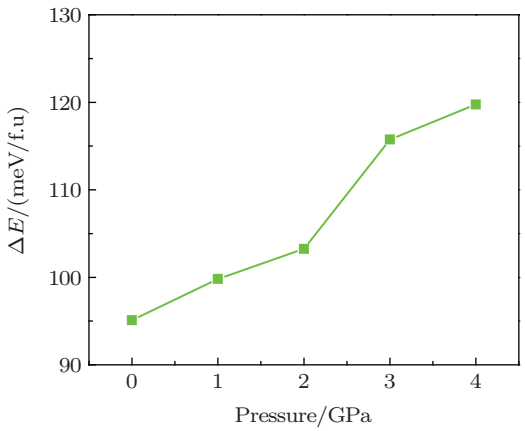


Fig. 4. (color online) Total energy difference between austenite and martensite states of Ni–Mn–Sn as a function of pressure.

To gain further insight into the origin of the pressure effects on the magnetic properties and the martensitic transformation in Ni–Mn–Sn, we take the electronic structures of Ni–Mn–Sn at ambient pressure and the applied pressure of 4 GPa for example. Figure 5 illustrates the densities of states (DOSs) for the austenite and martensite of Ni–Mn–Sn at ambient pressure. It can be seen that Mn 3d states of majority spin and minority spin are split with respect to the Fermi level. This distribution makes Mn mostly responsible for the magnetization. Moreover, it can be noted that the magnetic moment of Mn_{Sn} is antiparallel to that of Mn_{Mn}. The Ni 3d states have similar distributions for the majority spin and the minority spin, resulting in a rather small magnetization. The majority-spin DOS of Ni–Mn–Sn martensite is similar to that of cubic austenite. However, when the cubic Ni–Mn–Sn austenite transforms into the tetragonal martensite, a significant reduction of the peak of the total minority-spin DOS at the Fermi level is clearly observed, which is due to the Ni 3d minority-spin states. Upon the martensitic transformation, the significant reduction of the peak can be attributed to the hybridization between the Ni 3d states and the 3d states of excess Mn atoms at the Sn sites. From Fig. 5(b), it can be noted that the magnetic moment of Mn_{Sn} is antiparallel to that of Mn_{Mn} in the martensite. Moreover, the occupied Mn_{Sn} 3d states are located on the lower energy side of the Ni 3d states in the minority-spin band. Then the hybridization between the Mn_{Sn} 3d and Ni 3d minority-spin states causes an energy shift of the Ni 3d bands toward the Fermi level and a reduction of the peak of the minority-spin DOS at the Fermi level, thereby lowering the electronic energy of the structure and making the tetragonal structure more stable than the cubic one.

Figure 6 shows the DOSs for austenite and martensite of Ni–Mn–Sn at the applied pressure of 4 GPa. It can be seen that the DOSs of Ni–Mn–Sn at ambient pressure and the applied pressure of 4 GPa are similar. However, it is worth noting that the application of the pressure leads to broadening of the Ni 3d bands, which stems from the decrease of the interatomic distances and therefore the increase of the overlap between the atomic states. One of the consequences of the band broadening is a trend toward the decrease of the magnetic moment. This trend is demonstrated in Fig. 1. The other consequence of the band broadening under an applied pressure is enhancing the hybridization between the Mn_{Sn} 3d and Ni 3d states in martensite, which makes the martensite more stable than the austenite, leading to an increase in the martensitic transformation temperature.

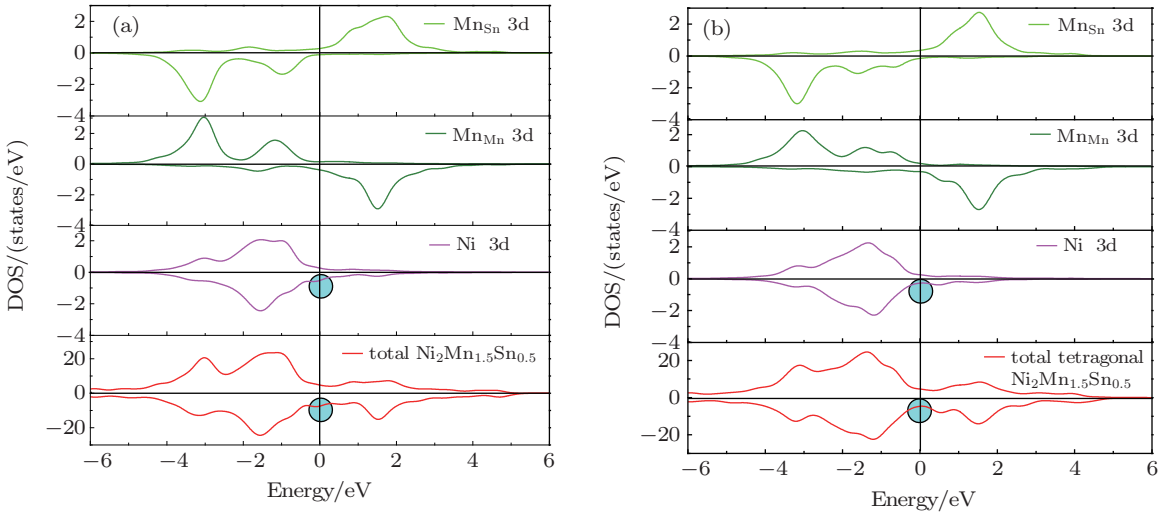


Fig. 5. (color online) DOSs for (a) austenite and (b) martensite of Ni–Mn–Sn at ambient pressure.

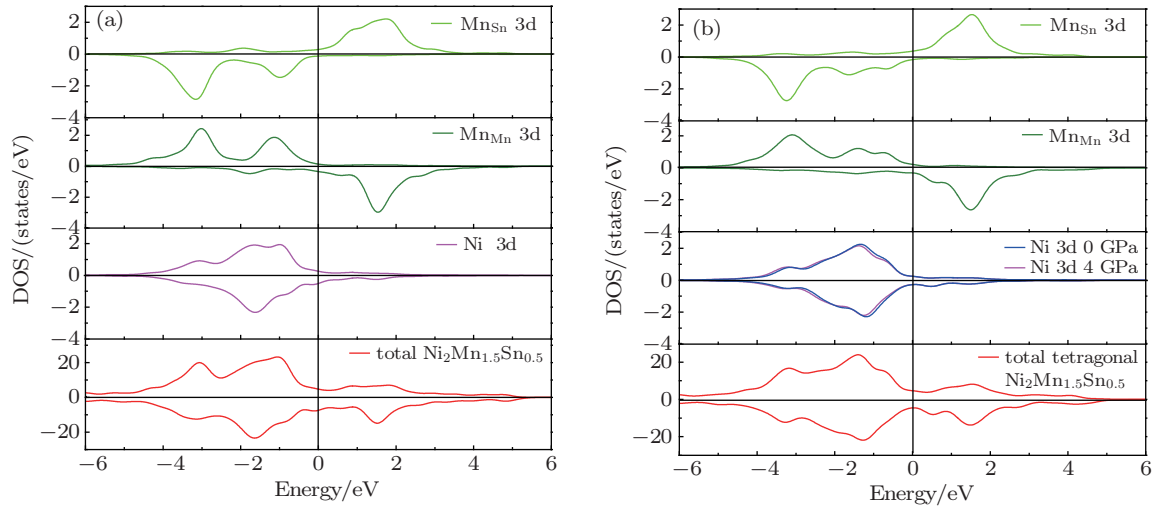


Fig. 6. (color online) DOSs for (a) austenite and (b) martensite of Ni–Mn–Sn at an applied pressure of 4 GPa.

4. Conclusion

In this paper, the first-principles calculations are used to investigate the mechanism of the pressure effects on the magnetic properties and the martensitic transformation of Ni–Mn–Sn. It is found that the total and the atomic magnetic moments of both austenite and martensite decrease with the increase of pressure, which is closely related to the decrease of the lattice constant and broadening of the energy bands. The total energy difference between paramagnetic and ferromagnetic states of the austenite increases with increasing pressure, which brings an enhancement of T_c. Moreover, the pressure increases the relative stability of the martensite with respect to the austenite, leading to the increase of the martensitic transformation temperature. This fact is attributed to the enhancement of the hybridization between Mn_{Sn} 3d and Ni 3d states in the martensite due to broadening of the Ni 3d bands under pressure.

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