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SHAPE MEMORY PROPERTY OF $Ni_{2+x}Mn_{1-x}Ga$ BASED ON ELECTRONIC STRUCTURES

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The electronic structures of the bulk and film of $Ni_{2+x}Mn_{1-x}Ga$ were calculated to study the effect of Ni composition and surface on the shape memory and magnetic properties. For the bulk, the total energy difference between the cubic and the tetragonal structure increase with increasing Ni composition. This corresponds to the increase of the structural transition temperature. In the film, the shape memory property may not be preserved because band narrowing on the surface stabilizes the cubic structure. However, the property is recovered with increasing thickness.

Key words: shape memory property, structural transition, electronic structure, $Ni_{2+x}Mn_{1-x}Ga$, thin film

1.INTRODUCTION

There are a large number of ternary compounds with the Heusler type structure ($L2_1$). Among these compounds, Ni_2MnGa is one of the very few compounds which are ferromagnetic shape memory alloys. The origin of the shape memory property is in the phase transition between the tetragonal and the cubic structure. The transformation comes from a contraction along the [010] direction of the cubic phase. The deformation is large (c/a=0.94) but the reduction of the volume is small (about 1 percent). Recently, it was shown experimentally that the structural transition is driven by a band Jahn Teller effect[1]. Moreover, interesting experimental results were observed in the system $Ni_{2+x}Mn_{1-x}Ga$ which show a remarkable and unique phenomenon[2-4]. The phase transition temperature (T_t) increases but the Curie temperature (T_c) decreases with increasing Ni composition. The two transition temperatures of T_t and T_c merge near the composition of x=2.0. These results suggest that we can change the shape of the alloy by not only temperatures but also external magnetic fields.

To study the exciting phenomena, the electronic structures of $Ni_{2+x}Mn_{1-x}Ga$ were calculated for the bulk with the cubic and the tetragonal structure. When we use the film for applications, it is an interesting problem to investigate whether the shape memory property is preserved in the film or not. Therefore, the electronic structures were also calculated for the films.

2. CRYSTAL STRUCTURE AND METHOD OF CALCULATION

In general, Heusler alloys with composition X_2YZ have the cubic structure of the $L2_1$ type. However, the ternary alloys of $Ni_{2+x}Mn_{1-x}Ga$ have a tetragonal structure at low temperatures and a cubic one at high temperatures. Among the systems $Ni_{2+x}Mn_{1-x}Ga$, we take up the cases x=0, 0.125 and 0.25 where the alloy is treated as an ordered alloy with the tetragonal group $O^1_{4h}(P_{4/m\ 2/m\ 2/m})$. The theoretical values of the lattice constant were determined by the lattice constant dependence of the total energy. For the tetragonal structure, the ratio of c/a was assumed to be 0.94 of the experimental value. The values for the cubic and tetragonal structures are 5.7635 Å and 5.8836 Å for x=0, 5.7386 Å and 5.8582 Å for x=0.125 and 5.729 Å and 5.849 Å for x=0.25. The values for x=0 are in good agreement with the experimental values of 5.825 Å and 5.920 Å.

We also take up the (001) films. There are two types of YZ and X planes in the films, where YZ plane contains Y(Mn) and Z(Ga) atoms and X plane X(Ni) atoms. We treat the films as super lattices which has a lattice constant a of $1/\sqrt{2}$ times of the bulk one. The lattice constant of c is assumed to be 40 times of the distance between the adjacent planes of the bulk perpendicular to the z axis. Two types of films are distinguished by the surface of YZ and X planes like SYZ5 and SX4, where the number means the number of the surface plane counted from the central plane. The description of films and planes are used in reference 5).

In order to calculate electronic structures, we use the LMTO-ASA method and the LSD approximation.

3. RESULTS FOR THE BULK

The local density of sates (DOS) of Ni_2MnGa is shown in Fig. 1 where the Fermi level is shown by a vertical line. The solid curves are for the cubic structure and the dotted curves for the tetragonal ones. Since Mn atoms in the cubic structure are surrounded by eight Ni atoms, the DOS for the majority spin is of a typical one of the bcc transition metals with two large peaks. The main peaks of DOS are below the Fermi in the majority-spin while there is a large peak above the Fermi level in the minority-spin states. Therefore, the Mn atoms carry a large magnetic moment, on the other hand, it is found that the Ni moment is small. The shapes of the DOS of the

tetragonal structure are generally similar to the cubic ones but they change in detail owing to the transformation from the cubic to the tetragonal structure. Paying attention to the DOS of the minority-spin states of Ni, we notice that the DOS of tetragonal structure is situated in the lower energy region, compared with one of the cubic. It is also seen in the DOS of the minority spin states of Ni that the energy bands near the Fermi level are spread by lowering of symmetry and a band Jahn Teller effect occurs near the Fermi level. These stabilize the tetragonal structure.

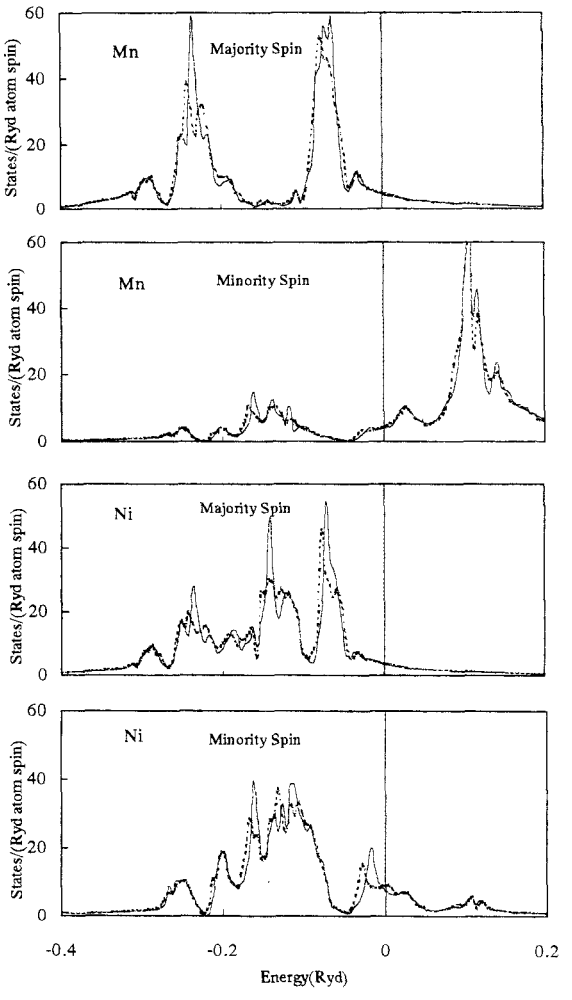

Fig.1 The local DOS of d-states of Ni and Mn in Ni2MnGa. The DOS of the cubic and the tetragonal structure are compared by solid and dotted curves. The Fermi level is shown by a vertical line and the DOS near the Fermi level is extended in the inset.

In the cases of x=0.125 and 0.25, there are Ni atoms in Mn sites of the case x=0 which are described as Ni(Mn) in the following. The local DOS of Ni(Mn) are shown in Fig.2. Comparing the DOS of Ni(Mn) in Fig.2 with the DOS of Ni in Fig.1, we notice that the DOS of Ni(Mn) is not similar to one of Ni but to one of the majority spin of Mn in Fig.1. The DOS of Ni(Mn) has a high peak near -0.05 Ryd and the one of the tetragonal structure is situated in the lower energy region, compared with the one of the cubic. Since the DOS of Ni has peaks near the high peak of Ni(Mn) but the DOS of Mn is low as seen in the case x=0, the hybridization between d-states of Ni(Mn) and the neighboring Ni in the case x=0.25 is stronger than the hybridization between d-states Mn and Ni in the case x=0. Thus, the high peak of Ni(Mn) effects on the peak of Ni near the Fermi level and the tetragonal structure is moreover stabilized by substituting Mn with Ni. In the cases of x=0.125, the similar features are seen.

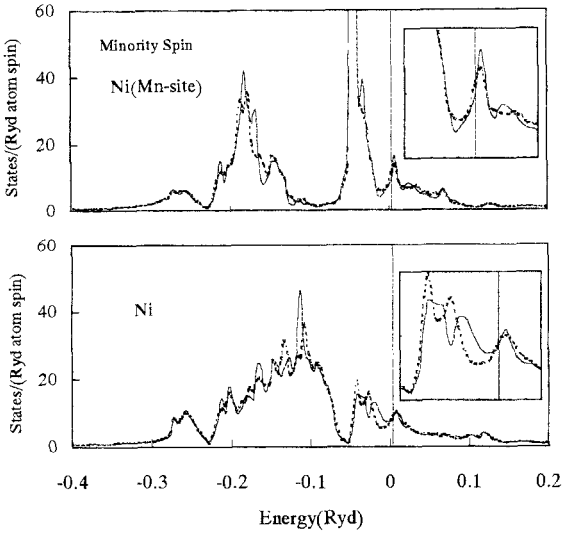

Fig.2 The local DOS of Ni(Mn) in Ni2+xMn1-xGa (x=0.25). The DOS of the cubic and the tetragonal structure are compared by solid and dotted curves.

As seen above, the DOS of $Ni_{2+x}Mn_{1-x}Ga$ change slightly in shape when the structural transformation takes place. This suggests that there is the difference of total energy between the cubic and the tetragonal structure. The value of the difference per formula unit is 0.8, 1.2 and 1.6 mRyd for the cases of x=0, 0.125 and 0.25, respectively. The energy is lower for the tetragonal structure than for the cubic, that is, it is expected that the tetragonal structure is stable at low temperatures as observed. When we convert the energy difference to the structural transition temperature, the transition temperature increases with increasing Ni composition. This corresponds to the experimental result.

4. RESULTS FOR THE FILM

Changing the thickness of films from SYZ3 with five layers to SYZ9 with seventeen layers, we calculated the electronic structures of the films for the cubic and tetragonal structures. The local DOS of SYZ9 film are shown in Fig.3 and Fig.4 for the majority-spin of Mn and the minority-spin of Ni, respectively. The solid and the dotted curve distinguish the DOS of the cubic and the tetragonal structure. Comparing the DOS of Mn on the different plane, we found that band narrowing occurs on the surface and the DOS of the tetragonal structure

generally shift to the higher energy region, compared with one of the cubic. The shift is smaller for the inner plane and the shape approaches to the one of the bulk. The similar feature is seen for the DOS of Ni. Thus, the surface has a tendency to stabilize the cubic structure. This is contrary to the fact that the tetragonal structure is more stable than the cubic structure at low temperatures. Therefore, it may be

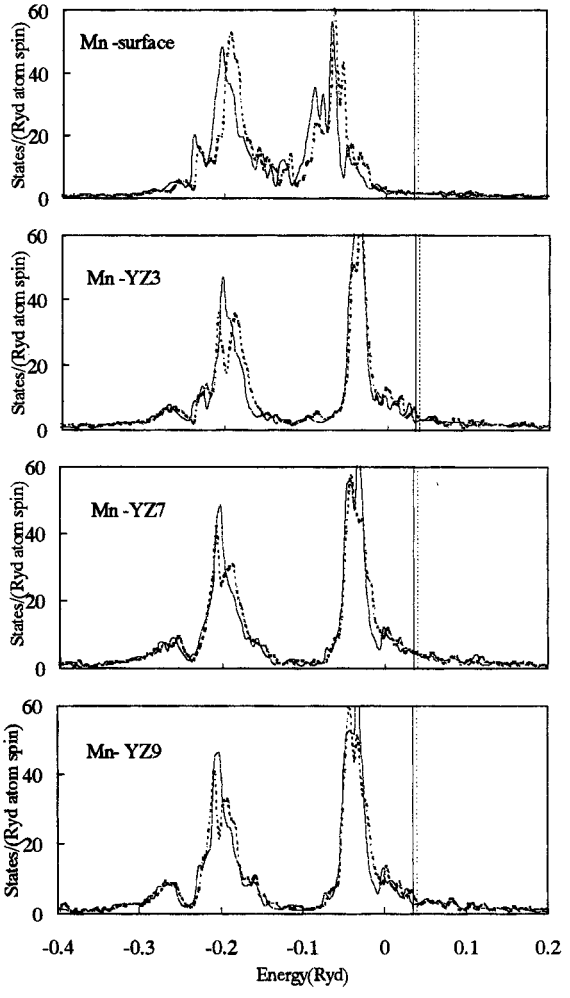

Fig.3 The local DOS of the majority-spin of Mn in SYZ9 film. The DOS of the cubic and the tetragonal structure are compared by solid and dotted curves on each plane.

difficult to preserve the shape memory property in the thin films.

However, paying attention to the DOS near the Fermi level of the minority-spin of Ni, we notice that the occupied states just below the Fermi level in the cubic structure partially move to the lower energy region in the tetragonal structure. That is, the structure of the DOS of the inner plane has a tendency to stabilize the tetragonal structure, as seen in the bulk. The tendency becomes stronger as the plane becomes far away from the surface.

The total energy difference between the cubic and the tetragonal structure is plotted as a function of the film thickness in Fig. 5. The absolute value decreases with increasing thickness. This reflects the features described above that the effect of the surface to stabilize the cubic structure is strong in the thin film and the effect of the Ni DOS of the inner plane to stabilize the tetragonal structure becomes strong with increasing thickness.

Since the number of neighbors of an atom on the surface is small, compared with an inside (or bulk)

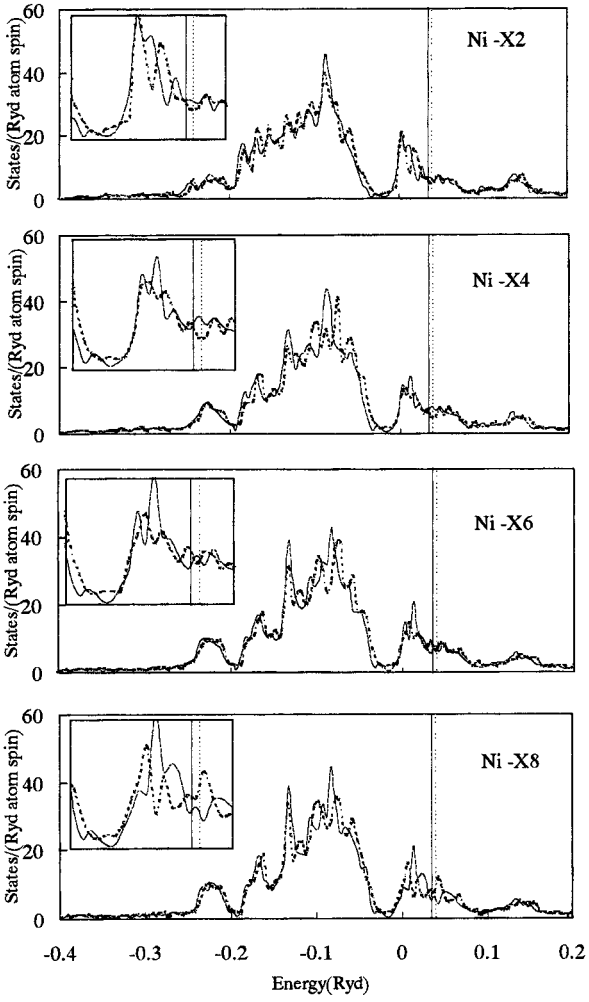

Fig.4 The local DOS of the majority-spin of Mn and the minority-spin of Ni in SYZ9 film. The DOS of the cubic and the tetragonal structure are compared by solid and dotted curves on each plane.

atom, band narrowing occurs as described above. The band tail of Mn atoms on the surface becomes small above the Fermi level in the majority-spin state and below the Fermi level in the minority-spin state. This drives the enhancement of the magnetic moment. The magnetic moments on the Mn atoms are enhanced by 0.25 - 0.66μ_B, compared with the tetragonal bulk values of 3.27μ_B. The theoretical value (3.75μ_B per formula unit) for the bulk with the tetragonal structure is slightly larger than one observed by P.J. Brown [1] and equal to one observed by T. Kanomata [6].

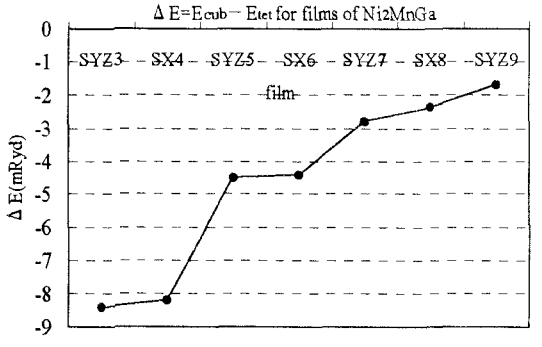

Fig.5 The total energy difference between the cubic (Ecub) and the tetragonal structure (Etet) for films of Ni2MnGa.

SUMMARY

The total energy difference between the cubic and the tetragonal structure were calculated for the bulk and the film of Ni2+xMn1-xGa. For the bulk, the composition dependence of the difference corresponds to the one of the structural transition temperature. The electronic structures of the thin films suggest that the shape memory property may not be preserved because of the band narrowing on the surface. However, the property may be recovered with increasing thickness. The recovery is mainly brought by the electron redistribution due to lowering of symmetry. A band Jahn Teller effect partially contributes to the recovery.

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