Electronic Structure and Magnetic Properties of Ferromagnetic Shape Memory Alloys CoNiAl*¹

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To expand our knowledge of electronic structures and magnetic properties for ferromagnetic shape memory Co-Ni-Al alloys, which undergo a thermoelastic martensitic transformation from a $B2$ to an $L1_0$ structure, we have performed first-principles band calculations for the composition of Co:Ni:Al = 1:1:1, *i.e.*, $(\text{Co}_{1/3}\text{Ni}_{2/3})(\text{Co}_{1/3}\text{Al}_{2/3})$ and $(\text{Ni}_{1/3}\text{Co}_{2/3})(\text{Ni}_{1/3}\text{Al}_{2/3})$. Their electronic structures have been calculated for the supercell structure, including a cubic-tetragonal distortion and a spin polarization. The obtained total energy indicates that $(\text{Co}_{1/3}\text{Ni}_{2/3})(\text{Co}_{1/3}\text{Al}_{2/3})$ may be more appropriate than $(\text{Ni}_{1/3}\text{Co}_{2/3})(\text{Ni}_{1/3}\text{Al}_{2/3})$. In the paramagnetic state of $(\text{Co}_{1/3}\text{Ni}_{2/3})(\text{Co}_{1/3}\text{Al}_{2/3})$, it has been found that the transformation from the $B2$ to the $L1_0$ structure comes from the change of the environment of the Co atoms (Co[2e]) on the original Al sites and, other Co and Ni atoms. These features are reflected in their d -orbital density of states (DOS). The Co[2e] atoms also play an important role in the magnetic transition between the paramagnetic and ferromagnetic states. The Co[2e] atoms carry magnetic moments corresponding to those of fcc Co (hcp Co) and the energy gain due to the spin polarization is brought. The origin of the spin polarization can be attributed to the similarity of their environment. This is confirmed by the similarity of their d -orbital DOS s. The “band energy” estimated from total DOS shows that the changes of DOS near the Fermi level bring the band-Jahn-Teller-type stabilization of the distorted structure.

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1. Introduction

The ferromagnetic shape memory alloys (FSMAs) attract a great deal of attention due to the fact that the shape memory effect can be controlled by applying magnetic field in addition to conventional controls by temperature and/or stress.

Recently, Co-Ni-Al alloys have been developed as new FSMAs.^{1–3)} Oikawa *et al.*¹⁾ have investigated Co-Ni-Al alloys and have shown the following facts. (1) A system of ferromagnetic β phase Co-Ni-Al alloys with the $B2$ structure exhibits the shape memory effect. (2) The alloys with the composition range (30–45 at%)Co-Ni-(27–32 at%)Al undergo a paramagnetic/ferromagnetic transition as well as a thermoelastic martensitic transformation from the β ($B2$) to the β' ($L1_0$) phase. (3) The Curie and the martensitic start temperatures in the β phase can be controlled independently to fall within the range of 120–420 K.

To expand our knowledge of electronic structures and magnetic properties for ferromagnetic shape memory Co-Ni-Al alloys, we have performed first-principles band calculations for the composition of Co:Ni:Al = 1:1:1, *i.e.*, $(\text{Co}_{1/3}\text{Ni}_{2/3})(\text{Co}_{1/3}\text{Al}_{2/3})$ and $(\text{Ni}_{1/3}\text{Co}_{2/3})(\text{Ni}_{1/3}\text{Al}_{2/3})$. Their electronic structures have been calculated for the supercell structure, including a cubic-tetragonal distortion and a spin polarization.

Band calculations have been performed by the linear muffin-tin orbital atomic sphere approximation (LMTO-ASA) method⁴⁾ within a local spin density approximation (LSDA).^{5,6)} The ratio of atomic sphere radii is determined by

trial and error to satisfy the charge-neutrality requirement for each atom. The value is 1.00(Co):0.99(Ni):1.08(Al).

The contents of this paper are as follows. In §2, we will explain the adopted supercell structure. In §3, we will show electronic structures and magnetic properties obtained from band calculations and discuss the stabilization of the ferromagnetic state and the distorted structure. This paper comes to a conclusion in §4.

2. Model Structure

We assume the crystal structures of Co-Ni-Al alloys as follows. Figure 1 shows two supercells for the austenite and martensite structure (SC_A and SC_M), both of which have a tetragonal symmetry of the space group $P4/mmm$.⁷⁾ The austenite supercell (SC_A) is composed of three unit cells of the cubic $B2$ structure, *i.e.* 6 atoms (4 inequivalent sites) per cell (see Table 2).

In this paper, we will use $a = a_M$ and $c = c_M/3$, where a_M and c_M denote the lattice constants of the martensite supercell (SC_M). If a_A and c_A denote the lattice constants of the SC_A , then $a = \sqrt{2}a_A$ and $c = c_A/3$. Thus, the SC_M with $c/a = 1/\sqrt{2}$ (≈ 0.707) is equivalent to the undistorted structure.

Table 1 shows the first and second neighboring sites of each site in the SC_M with $c/a \neq 1/\sqrt{2}$. Table 2 shows the occupancies of inequivalent sites in the supercell for $(\text{Co}_{1/3}\text{Ni}_{2/3})(\text{Co}_{1/3}\text{Al}_{2/3})$ and $(\text{Ni}_{1/3}\text{Co}_{2/3})(\text{Ni}_{1/3}\text{Al}_{2/3})$. The models for $(\text{Co}_{1/3}\text{Ni}_{2/3})(\text{Co}_{1/3}\text{Al}_{2/3})$ and $(\text{Ni}_{1/3}\text{Co}_{2/3})(\text{Ni}_{1/3}\text{Al}_{2/3})$ are named as CNCA and NCNA, respectively.

Before we will show results, we make some comments. Paramagnetic electronic structures of NiAl and CoAl have been calculated for the conventional cubic $B2$ structure and the above-mentioned supercell structures (SC_A and SC_M). Then, we have made sure that there hardly exist differences among those in the points of the total energy per formula unit

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Fig. 1 Supercells corresponding to the martensite phase. The cell showed by the broken line corresponds to the austenite phase.

Table 1 First and second atomic configuration in the SC_M with $c/a \neq 1/\sqrt{2}$.

Site	First neighbor	Second neighbor
1a	8(4i) ^a	4(1c)
1c	8i(4i)	4(1a)
2g	4(4i) 4(2e)	4(2h)
2h	4(4i) 4(2e)	4(2g)
2e	4(2g) 4(2h)	4(2e)
4i	2(1a) 2(1c) 2(2g) 2(2h)	4(4i)

a) For example, "8(4i)" means that the atom at the 1a site has 8 atoms at the 4i site in the first neighbor.

Table 2 Occupancies of inequivalent sites in two supercells, SC_A and SC_M .

Name	Site and atom				Numbers of atom		
SC_A	1a	2g	1d	2h			
SC_M	1a 1c	2g 2h	2e	4i	Al	Ni	Co
CNCA ^a)	Co	Ni	Co	Al	4	4	4
NCNA ^b)	Ni	Co	Ni	Al	4	4	4

a) CNCA corresponds to $(Co_{1/3}Ni_{2/3})(Co_{1/3}Al_{2/3})$.

b) NCNA corresponds to $(Ni_{1/3}Co_{2/3})(Ni_{1/3}Al_{2/3})$.

(f.u.) and the lattice constant estimated from the minimum of the total energy. This fact may allow us safely to regard the SC_M with $c/a = 1/\sqrt{2}$ as the austenite structure corresponding to the cubic $B2$ structure.

3. Results and Discussion

3.1 Total energy, c/a and magnetic moment

Figure 2 shows the results of total energy (E) vs tetragonality (c/a) for CNCA and NCNA in the paramagnetic (P) and ferromagnetic (F) states, where E is total energy per

Fig. 2 Total energy per u.c. (E) vs tetragonality (c/a) for CNCA and NCNA in the paramagnetic and ferromagnetic states.

unit cell (u.c.). Here we have done the following procedure. First, for each of the P and F states, we performed total-energy calculations changing the value of a with the fixed value of $c/a = 1/\sqrt{2}$ (corresponding to an undistorted structure) and then determined the lattice constant (or the volume v_0) which minimizes the total energy. Next, we performed total-energy calculations changing the value of c/a with the fixed value of v_0 , and then determined the c/a which minimizes the total energy. The obtained value of c/a are 0.753 and 0.775 (0.784 and 0.743) for the P and F states of CNCA (NCNA), respectively. The c/a ratio for the F state of CNCA is about 5% smaller than the experimental value ($c/a = 0.816$) for 33Co-Ni-28Al.⁸⁾

Figure 2 indicates that CNCA is more appropriate than NCNA because the total energy of CNCA is lower than that of NCNA in both cases of P and F states. Therefore, we pay attention to CNCA in the following. The results for total energies of CNCA suggest the following transformation in the Co-Ni-Al alloys with the composition of Co:Ni:Al = 1:1:1. A paramagnetic austenite phase transforms into a ferromagnetic martensite phase via a paramagnetic martensite phase on cooling. This type of magnetic and martensitic transformation has been observed in Co-Ni-29 at%Al¹⁾ and Co-Ni-30 at%Al,²⁾ where combinations of magnetic transformation and martensitic transformation are grouped into three types from the results of the composition dependency of the Curie temperature, the martensitic transformation temperature and the austenitic finishing temperature. In order to understand (or discuss) this interesting composition dependency, we must perform band calculations for several compositions. This investigation is in progress. Then, the discussion for the composition dependency will be postponed until the finish of those band calculations.

The obtained magnetic moments on each atomic site are listed in Table 3, where there hardly exist differences in values of the magnetic moments between the 1a and 1c (2g and 2h) sites and therefore one value is listed for the sites.

Table 3 shows that the Co atoms (Co[2e]) on the 2e site, which is occupied by the Al atoms in the $B2$ -type NiAl alloy, play an important role in the magnetic transition between the P and F states. The Co[2e] atoms carry magnetic moments $1.70\mu_B$ corresponding to those of fcc Co (hcp Co) and the

Table 3 Magnetic moments in CNCA.

	Moments (μ_B)			
	1a/1c	2g/2h	2e	4i
$c/a = 1/\sqrt{2}$	-0.071	0.177	1.645	-0.009
$c/a = 0.775$	-0.029	0.261	1.696	-0.010

energy gain due to the spin polarization is brought. (Our calculated data for fcc Co and hcp Co with $c/a = 1.633$ are 1.66 and $1.60\mu_B$, respectively.) This can be attributed to the similarity of their environment. As shown in Table 1, the Co[2e] atom has 8 Ni and 4 Co atoms in the first and second nearest neighbor, respectively. The distance from Co[2e] to Co atoms is about 10% longer than that to the Ni atom. Thus, the Co[2e] atom has a similar environment to fcc Co or hcp Co. This mainly causes the spin polarization (spin magnetization) of the Co[2e] atom. This fact is also confirmed by the similarity of their d -orbital density of states (DOS). (The d -orbital DOS of Co[2e] is shown in the next subsection but that of fcc or hcp Co is not shown in this paper. The d -orbital DOS of fcc Co, for example, can be seen in Ref. 9.).

3.2 Density of states

Figure 3 shows total density of states ($TDOS$) of CNCA in the P and F states. In this figure, the $TDOS$ s for undistorted ($c/a = 1/\sqrt{2}$) and distorted ($c/a = 0.775$) cases are shown. Each contribution to the $TDOS$ from the partial DOS ($PDOS$) of each constituent atom can be understood from Fig. 4, where the symbol Co(d), for example, means the d orbital of the Co atom. In Fig. 4, we do not show the d -orbital DOS of the Co atom on the 1c site (Co[1c]) because its shape is very similar to that of the Co atom on the 1a site (Co[1a]). The same situation is occurred in case of d -orbital DOS s for the Ni[2g] and Ni[2h] atoms.

From Fig. 3, we can see the $TDOS$'s change brought from the distortion. Though there are several portions that the change is remarkable, it is particularly important that the change in the P state between -0.2 aJ and E_F , where Co[2e] and Ni[2g] atoms have large peaks in their $PDOS$ s as shown

Fig. 3 $TDOS$ (States/(f.u. spin)) of CNCA in the paramagnetic and ferromagnetic states. $TDOS$ s for the undistorted and the distorted structure are shown by the broken and solid lines. The Fermi level for the distorted structure is shown by the vertical broken line.

Fig. 4 $PDOS$ (States/(atom spin)) of CNCA in the paramagnetic and ferromagnetic states. $PDOS$ s for majority-spin and minority-spin electrons are shown by the solid and broken lines. The Fermi level is shown by the vertical broken line.

in Fig. 4. (The reason for being important will be explained in the next subsection.)

Figure 4 shows that the Co[2e] atom has a large peak at the Fermi level (E_F) in the P state. This fact suggests that the Co[2e] atom carries a magnetic moment due to a spin polarization. This is confirmed by the result shown in Table 3, as already mentioned, and the $PDOS$ of the F state shown in Fig. 4.

3.3 Band energies

We have estimated the band energy of each constituent atom from its $PDOS$ in order to quantitatively investigate the $PDOS$'s change brought from the distortion. The band energy (E_b) is written as $E_b = \int_{-\infty}^{E_F} \epsilon D(\epsilon) d\epsilon$, where $D(\epsilon)$ denotes $PDOS$ at an energy ϵ .

The results for CNCA are shown in Fig. 5, where, "P-P" ("F-F") means the band-energy difference (ΔE_b), i.e., $\Delta E_b = E_b(\text{distorted}) - E_b(\text{undistorted})$, for the paramagnetic

Fig. 5 Band-energy difference per atom ($\Delta E_b(\text{atom})$) between the undistorted and the distorted structure for the paramagnetic and the ferromagnetic state.

(ferromagnetic) state. Moreover, the symbol “Co[1a/1c]”, for example, means that the value of ΔE_b is the average of those for the Co[1a] and Co[1c] atoms.

Figure 5 shows that the band energies of Ni[2g/2h] and Co[2e] are negative, while that of Co[1a/1c] is positive. The band energy of Al[4i] is positive but negligible. Since the band-energy gain per cell are 0.12 and 0.33 aJ for the P and F states, respectively, the band-energy gain of Ni[2g/2h] and Co[2e] exceeds the loss of Co[1a/1c] and Al[4i] in both states. The origin of the band-energy gain of the Ni[2g/2h] and Co[2e] atoms mainly attributes to the change of their environment, which comes from the transformation from the undistorted to the distorted structure.

The band-energy dependency on energy can be seen in Fig. 6, where enlarged d -orbital DOS s near E_F are also shown. It is notable that the band-energy difference per formula unit ($\Delta E(f.u.)$) becomes zero at an energy (E_0) between -0.2 aJ and E_F , and afterward becomes negative in the P state. This suggests the band-Jahn-Teller effect in the $PDOS$ s of the Co[2e] and Ni[2g] atoms. That is, the $PDOS$'s peaks near E_F of the Co[2e] and Ni[2g] atoms are split (or broadened) owing to lowering of the symmetry, when the crystal structure changes from the cubic to the tetragonal structure. This is confirmed by their enlarged d -orbital DOS s near E_F shown in Fig. 6. Though the $PDOS$'s peak of the Co[1a] atom is separated from E_F , its split or broadened effect also contributes to the above behaviour of $\Delta E(f.u.)$ near E_F .

4. Conclusion

Using a supercell method, we have performed first-principles band calculations for the composition of Co:Ni:Al = 1:1:1, *i.e.*, $(\text{Co}_{1/3}\text{Ni}_{2/3})(\text{Co}_{1/3}\text{Al}_{2/3})$ and $(\text{Ni}_{1/3}\text{Co}_{2/3})(\text{Ni}_{1/3}\text{Al}_{2/3})$. The total energy indicates that $(\text{Co}_{1/3}\text{Ni}_{2/3})(\text{Co}_{1/3}\text{Al}_{2/3})$ is more appropriate than $(\text{Ni}_{1/3}\text{Co}_{2/3})(\text{Ni}_{1/3}\text{Al}_{2/3})$. The result of total energies of the former model

Fig. 6 Band-energy dependency on energy (left) and $PDOS$ s of the undistorted and the distorted structure near the Fermi level (right). In the left, $\Delta E_b(\text{atom})$ and $\Delta E_b(f.u.)$ show band-energy differences per atom and that per f.u., respectively. In the right, d -orbital DOS s for the undistorted and the distorted structure are shown by the broken and solid lines. The Fermi level for the distorted structure is shown by the vertical broken line.

structure (CNCA) suggests the following transformation; A paramagnetic austenite phase transforms into a ferromagnetic martensite phase via a paramagnetic martensite phase on cooling.

The structural transformation in the P state comes from the band-Jahn-Teller effect. This is reflected in the band energy and the $TDOS$ near E_F .

The spin polarization of the Co[2e] atom brings the energy gain and causes the magnetic transition from the paramagnetic to the ferromagnetic state in CNCA.

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