



# Ab initio study for magnetism in Ni<sub>2</sub>MnAl full-Heusler alloy: A cluster expansion approach for total energy

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## ABSTRACT

We show the accuracy and convergence of our ab initio real-space cluster expansion (CE) approach for total energies of alloys, which is useful for the study of atomic structures and magnetism of A-rich AX<sub>2</sub> full-Heusler alloys such as Ni<sub>2</sub>MnAl. In the present CE, each and every term is uniquely determined by the combination of total energies of X and Y impurities in A metal with a total energy of A metal (per atom), all of which are accurately calculated by the full-potential KKR program combined with the generalized gradient approximation in the density functional formalism. We show that the magnetic energy of Ni<sub>2</sub>MnAl is reproduced very well by the present CE, from a dilute limit, including up to the 4-body interaction energies of Mn and Al impurities in Ni-bcc metal.

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## 1. Introduction

Ferromagnetic (FM) full-Heusler alloys with L<sub>21</sub> structure have attracted a great deal of interest during the last century as materials of various high qualities [1–3]. For examples, Co<sub>2</sub>MnSi is expected as a half-metallic (100% spin-polarization at the Fermi level) FM alloy with high Curie temperature, while Ni<sub>2</sub>MnAl as a FM shape memory alloy. According to the band calculations, both the ground states of Co<sub>2</sub>MnSi and Ni<sub>2</sub>MnAl are FM and Co<sub>2</sub>MnSi is half-metallic [4–6]. However, the experimental results are different from the band calculation results: the spin-polarization of only 50–60% for Co<sub>2</sub>MnSi and the anti-FM state for Ni<sub>2</sub>MnAl at elevated temperatures [3,7–9]. The decrease of spin-polarization may be due to the defects in Co<sub>2</sub>MnSi, as being discussed in this conference, and the change of magnetism of Ni<sub>2</sub>MnAl (from FM to AFM) may be caused by the atomic rearrangement from L<sub>21</sub> to B<sub>2</sub>, which occurs at elevated temperatures [6,9].

Thus, the development of the electronic devices of high qualities needs the theoretical study of the magnetism of the full-Heusler alloys with and without defects.

We have recently proposed the ab initio cluster expansion (CE) approach [10,11] for the total energies of ordered and disordered alloys, and have shown that the relative stability of atomic structures (L<sub>12</sub> and DO<sub>22</sub> of Al<sub>3</sub>X (X = Sc, Ti, V)) and magnetism (FM and AFM of Ni<sub>2</sub>MnAl) are understood by considering only the low-order

terms in the present CE, such as the 2-body and 3-body interaction energies (IEs) [6,10,11]. Thus, it is obvious that the present CE is very useful, at least, to study qualitatively the stability of atomic structures and magnetism of ordered and disordered alloys.

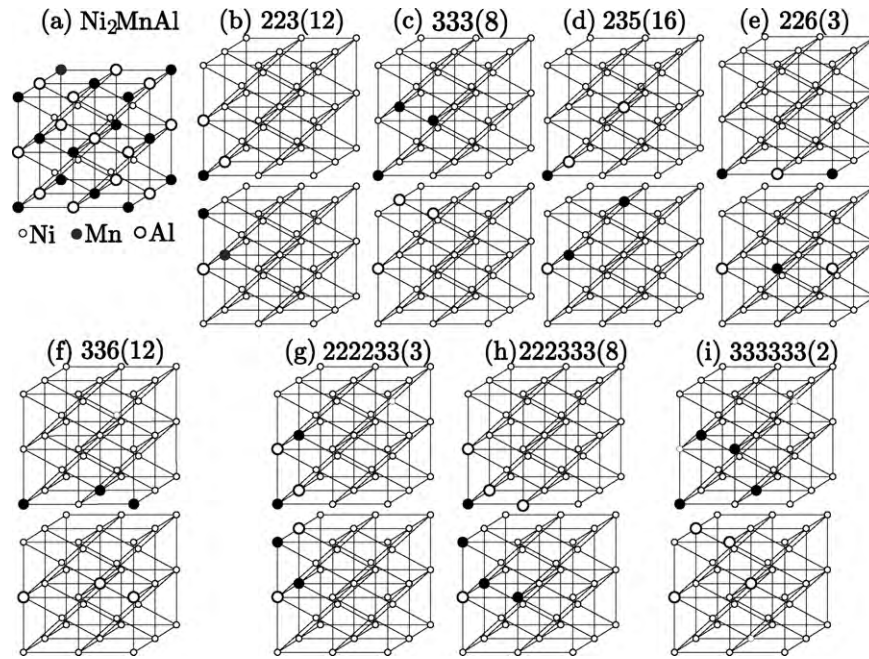
In order to study quantitatively the atomic structures and magnetism of full-Heusler alloys, however, it is necessary to know the accuracy and convergence of the present CE for total energies of alloys. We very recently found that the band calculation results for total energies of A-rich AX binary alloys in the ordered phase, such as Al<sub>3</sub>Sc and Fe<sub>3</sub>Al (25% concentration of X impurity element) and magnetic energies of A-rich AX<sub>2</sub> ternary alloys such as Ni<sub>2</sub>MnAl (50% concentration of X and Y impurities) are reproduced very well by the present CE, from a dilute limit, including up to 4-body IEs among neighboring impurities in A metal.

In the present paper, we show the calculated results for the Ni<sub>2</sub>MnAl and demonstrate that the present CE is useful even for the quantitative discussion of magnetism in Ni<sub>2</sub>MnAl, although some results [12] for Al<sub>3</sub>Sc and Fe<sub>3</sub>Al are also shown for a comparison. It is noted that the present work for Ni<sub>2</sub>MnAl may be a stringent test for the applicability of the present CE.

## 2. Method of ab initio calculations

The calculations for total energies of impurity systems are based on the density functional formalism in the generalized gradient approximation (GGA) [6,11,13]. In order to solve the Kohn–Sham equations, we use a multiple scattering theory in the form of the KKR Green's function method for full potentials [13].

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**Fig. 1.** Atomic arrangements for L21 structure of Ni<sub>2</sub>MnAl (a), and for 3-body (b–f) and 4-body (g–i) interaction energies (IEs) of Mn and Al impurities in Ni-bcc metal. The numbers of 3-body and 4-body IEs per unit cell are shown in parentheses. See the text for details.

The advantage of the Green's function method is that by introducing the host Green's functions, the embedding of impurities in an otherwise ideal crystal is described correctly, differently from the usual super-cell calculations.

In the present calculations for impurity systems in the bcc structure, only the potentials up to the 2nd-neighbors around impurities are re-determined self-consistently because the potential perturbation due to the insertion of impurities in metals is localized in the vicinity of impurities, as shown in Ref. [13]. The number of perturbed atoms up to the 2nd-neighbors around a single impurity is 15, thus the maximum numbers of the perturbed atoms, being taken into account in the present calculations, are not larger than 30, 45, and 60 for two, three, and four impurity systems, respectively. On the other hand, the change of the wave functions due to the insertion of impurities is delocalized over the whole space. It is noted that the total energy change due to the perturbed wave functions over the infinite space is correctly evaluated by using the Lloyd's formula [13].

The total energies and the Green's functions of A metal are calculated by the screened version of KKR calculations, in which the short-range structural Green's functions make the numerical calculation very rapid and efficient [6,11,14,15]. In order to calculate total energies in the GGA formalism, we use the electronic densities obtained self-consistently by the local-spin-density-approximation (LSDA) calculations for simplicity. The accuracy of the present GGA calculations is also discussed in Ref. [16].

### 3. Cluster expansion approach from a dilute limit

The characteristic feature of the present CE for total energies of A-rich AXY alloys is that all the terms in the present CE are uniquely determined by the combination of total energies at different atomic arrangements of X and Y impurities in A metal with the total energy of A metal (per atom) [10,11,17–19]. The present CE is very different from the Connolly-Williams approach where all the terms in the CE are the adjustable parameters, being determined via the fitting to the total energies of selected ordered alloys [20]. The CE for the

total energy of Ni<sub>2</sub>MnAl alloy is written as follows:

$$E_{\text{Ni}_2\text{MnAl}}^{\text{band}} = 2 \times E_{\text{Ni}}^{\text{band}} + E_{\text{Mn in Ni}} + E_{\text{Al in Ni}} + \Delta E_{\text{int}}^{2\text{-body}} + \Delta E_{\text{int}}^{3\text{-body}} + \Delta E_{\text{int}}^{4\text{-body}} + (\text{many-body IEs beyond 4-body}) \quad (1)$$

where the 1st-term is  $2 \times$  total energy of Ni atom in Ni-bcc metal (0-body of impurities), and the  $i$ -th ( $i=2,3$ ) terms are total energies of single X impurity ( $X=\text{Mn}$  or  $\text{Al}$ ), in Ni-bcc metal (including 1-body of impurities). The  $i$ -th terms ( $i=4-6$ ) are, respectively, the sum totals of  $n$ -body ( $n=2-4$ ) IEs of  $n$  impurities in Ni-bcc metal. The atomic arrangements of  $n$  ( $n=3,4$ ) impurities, used for the calculations of  $n$ -body IEs, are shown in Fig. 1, as discussed in the following section. The 1st-term is obtained by the present screened KKR calculations for Ni host [6]. The  $i$ -th ( $i=2,3$ ) terms are calculated accurately by the present program for impurity systems and include the IEs of single X impurity with the surrounding Ni-host atoms (1-body of X impurities) and the total energies of an isolated X impurity [21,22]. It is also noted that the energy change of the surrounding Ni atoms, caused by the replacement of single X impurity with a Ni atom, is also included accurately in the  $i$ -th ( $i=2,3$ ) terms, as discussed in Ref. [21]. The  $i$ -th ( $i=2,3$ ) terms are related with the solution energies of single Mn and Al impurities in Ni metal [18,22]. The  $i$ -th terms ( $i=4-6$ ) are, respectively, the 2-body IEs of Mn–Mn, Mn–Al, Al–Al in Ni ( $i=4$ ), the 3-body IEs of Mn–Mn–Mn, Mn–Mn–Al, Mn–Al–Al, Al–Al–Al in Ni ( $i=5$ ), the 4th-body IEs of Mn–Mn–Mn–Mn, Mn–Mn–Mn–Al, Mn–Mn–Al–Al, Mn–Al–Al–Al, Al–Al–Al–Al in Ni ( $i=6$ ), as discussed in the following section. The definitions of these IEs are given in Ref. [17,19].

### 4. Calculated results for Ni<sub>2</sub>MnAl

The calculated results for ferromagnetic (FM) and nonmagnetic (NM) states of Ni<sub>2</sub>MnAl (50% of impurity elements), corresponding to the states with and without the spin-polarization effect, are shown in Table 1(a). In the present calculation the lattice parameter

**Table 1**

Convergence of ab initio real-space cluster expansion for total energies (in Ry) of (a) an  $A_2XY$  alloy ( $Ni_2MnAl$  ternary alloy at  $L2_1$  structure) and (b)  $A_3X$  binary alloys ( $Al_3Sc$  at  $L1_2$  structure and  $Fe_3Al$  at  $DO_3$  structure). The lattice parameters used in the calculations were fixed to be 11.6 a.u., 7.6 a.u., and 5.4 a.u., respectively, for  $Ni_2MnAl$  ( $L2_1$ ),  $Al_3Sc$  ( $L1_2$ ), and  $Fe_3Al$  ( $DO_3$ ). The results of ferromagnetic (FM) and nonmagnetic (NM) states are shown for  $Ni_2MnAl$ . The contribution from each term is shown in parentheses. The exact results, obtained by the band calculations, are also shown for a comparison. See the text for details.

	FM	NM
(a) $Ni_2MnAl$ ternary alloy (A = Ni, X = Mn, Y = Al)		
0-body ( $2 \times E_A^{band}$ )	−6084.6216 ( $2 \times -3042.3108$ )	−6084.6141 ( $2 \times -3042.3070$ )
Up to 1-body ( $E_{X \text{ in } A}$ ) ( $E_{Y \text{ in } A}$ )	−8888.5201 (−2317.9188) (−485.9797)	−8888.4242 (−2317.8125) (−485.9976)
Up to 2-body ( $\Delta E_{int}^{2-body}$ )	−8888.5393 (−0.0192)	−8888.4147 (0.0095)
Up to 3-body ( $\Delta E_{int}^{3-body}$ )	−8888.5269 (0.0125)	−8888.3987 (0.0160)
Up to 4-body ( $\Delta E_{int}^{4-body}$ )	−8888.5281 (−0.0012)	−8888.4036 (−0.0048)
Exact	−8888.5259	−8888.3996
	A = Al, X = Sc	A = Fe, X = Al
(b) $A_3X$ binary alloys ( $Al_3Sc$ , $Fe_3Al$ )		
0-body ( $3 \times E_A^{band}$ )	−1457.5929 ( $3 \times -485.8643$ )	−7638.6742 ( $3 \times -2546.2247$ )
Up to 1-body ( $E_{X \text{ in } A}$ )	−2986.5753 (−1528.9824)	−8124.5873 (−485.9131)
Up to 2-body ( $\Delta E_{int}^{2-body}$ )	−2986.6148 (−0.0395)	−8124.5923 (−0.0050)
Up to 3-body ( $\Delta E_{int}^{3-body}$ )	−2986.6247 (−0.0099)	−8124.5943 (−0.0021)
Up to 4-body ( $\Delta E_{int}^{4-body}$ )	−2986.6247 (0.0000)	−8124.5943 (0.0000)
Exact	−2986.6221	−8124.5961

(see Fig. 1(a)) is fixed to be 11.6 a.u., being a little bit longer than the equilibrium lattice parameter (11.0 a.u.) [6]. For a comparison, the calculated results for  $Al_3Sc$  and  $Fe_3Al$  (25% of impurity elements), obtained by the same way in the present work, are also shown in Table 1(b). The detailed results for  $Al_3Sc$  and  $Fe_3Al$  will be published elsewhere [12]. We may usually expect that the interactions between the distant sites are less important than those between the near sites, and that the interactions including many sites are less important than the interactions involving the fewer sites. According to our experiences, the 2-body interactions are usually very long-ranged and the contribution from the many-body interactions beyond the 4-body is very small [11, 18, 19]. Thus, in the present CE for the total energy of  $Ni_2MnAl$ , we include the 2-body IEs up to the 20th neighbors and the terms up to 4-body IEs among the neighboring impurities. For example,  $\Delta E_{int}^{2-body}$  in Table 1 is the sum of  $n$ -th neighbor IE multiplied by a number of  $n$ -th pairs per unit cell. It is noted that there are three kind pairs (Mn–Mn, Al–Al and Mn–Al in Ni-bcc metal). The Mn–Mn and Al–Al pairs exist as the  $n$ -th pairs ( $n = 3, 6, 9, 11, 14, 17, 20$ ) in Ni-bcc, while the Mn–Al pairs as the  $n$ -th ( $n = 2, 5, 8, 13$  (2 kinds), 16, 19) pairs in Ni-bcc. In Fig. 1, we show the atomic arrangements of Mn and Al impurities in Ni-bcc metal, being used for the calculations of 3-body and 4-body IEs. The numbers of  $n$ -body IEs per unit cell are also shown in Fig. 1. For example, the 3-body interaction among 3 impurities in Fig. 1(b), which may be the most important 3-body interaction, is written as 223 because the

triangle of 3 impurities includes two 2nd-neighbors and one 3rd-neighbor, and the number of this 3-body IEs (223), per unit cell is 12, as shown in a parenthesis of the expression 223 (12).

Now we discuss the calculated results for  $Ni_2MnAl$ . It is noted that the total energies obtained by the present CE including up to the 4-body IEs among impurities at near sites reproduce fairly well (within the error of 1 mRy per atom) the band calculation results which correspond to the results obtained by the perfect CE, although the agreement is a little bit worse compared with the results (0.65 mRy and 0.45 mRy) obtained for  $Al_3Sc$  and  $Fe_3Al$ , as listed in Table 1(b). This may be easily understood because the concentration of impurity elements is larger for  $Ni_2MnAl$  (50% of impurity elements) than for  $Al_3Sc$  and  $Fe_3Al$  (25% of impurity element). It is also noted that the magnetic energy, being the energy difference between the band calculation results with and without the spin-polarization effect, is reproduced very well (within the error of 0.45 mRy per atom) by the present CE. This nice agreement may be understood by considering the localization character of magnetic interactions. It is also expected that the absolute errors in total energies, due to the neglect of many-body interactions beyond the 4-body, cancel because the magnetic energy is a total-energy difference between FM and NM states.

## 5. Summary

We showed that the magnetic energy of A-rich  $AXY$  ternary full-Heusler alloy ( $Ni_2MnAl$ ; A = Ni, X = Mn, Y = Al), being the system with the high concentration of X and Y impurities, is reproduced very well (within the error of 1 mRy per atom) by the present ab initio cluster expansion, from a dilute limit, including up to the 4-body interaction energies of X and Y impurities in A metal. This is a stringent test for the applicability of the present CE. Thus, we may conclude that the present CE is very useful even for the quantitative study of the atomic structures and magnetism in the full-Heusler alloys [6]. In order to study the temperature effect for the full-Heusler alloys, we now plan to carry out the molecular dynamic calculations with the accurate model potentials [23, 24] which are constructed via the fitting to the first-principles results obtained by the present CE.

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