Atomistic simulation of site preference, Curie temperature, and lattice vibration of $Nd_2Co_{7-x}Fe_x$*

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The effects of Fe substitution for Co on the structural stability and the site preference of intermetallics $Nd_2Co_{7-x}Fe_x$ with a hexagonal Ce_2Ni_7-type structure are studied by using a series of interatomic pair potentials. In $Nd_2Co_{7-x}Fe_x$, Fe atoms are substituted for Co atoms with a strong preference for the 6h sites and the order of site preference is 6h, 4e, 4f, 2a, and 12k. Calculated lattice parameters are found to be consistent with the reported results in the literature. The variation behaviour of the Curie temperature of $Nd_2Co_{7-x}Fe_x$ is explained qualitatively by the exchange interaction model. The properties related to lattice vibration, such as phonon density of states and Debye temperature, are first evaluated for the $Nd_2Co_{7-x}Fe_x$ compounds.

Keywords: interatomic potentials, site preference, crystal structure, lattice inversion

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1. Introduction

The magnetocrystalline anisotropies of rare-earth (or Y) transition metal intermetallic compounds have been studied by many researchers for their applications to permanent magnetic materials.[1−5] The series formally denoted by $R_{m+n}T_{2m+5n}$ (R and T represent the rare earth atoms and the transition metal atoms, respectively) has attracted much attention.[6−8] Compounds of this series are known to exist for RT_2 ($m = 1$ and $n = 0$), RT_3 ($m = 2$ and $n = 1$), RT_5 ($m = 0$ and $n = 1$), etc. The rare earth cobalt compound with a hexagonal Ce_2Ni_7-type structure or a rhombohedral Gd_2Co_7-type structure also belongs to a family $R_{m+n}T_{2m+5n}$, which is formed by the sequential stacking of m layers of Laves-phase RT_2 slabs and n layers of $CaCu_5$-type slabs alternately along the c direction.[6] The stacking of the slabs is accompanied by a shift of the layers, which gives rise to either hexagonal or rhombohedral symmetry.[7,8] The series formally denoted by $R_{m+n}T_{5m+3n} + B_{2n}$ has also attracted particular interest.[9−14] In the $R_{m+n}T_{5m+3n}B_{2n}$ series, the structural properties of the $R_2Co_7B_3$ series (for $m = 1$ and $n = 3$) with a $Ce_2Co_7B_3$-type structure and the $R_3T_{13}B_2$ series (for $m = 2$, $n = 1$) with a $Nd_3Ni_{13}B_2$-type structure have been reported in our previous work.[15,16] Now, we extend our study to the case of $R_{m+n}T_{2m+5n}$ compounds. In the present paper, we investigate the $m = 2$, $n = 2$ system with hexagonal symmetry, $Nd_2Co_{7-x}Fe_x$. The effects of Fe substitution on the phase stability and site preference of $Nd_2Co_{7-x}Fe_x$ are investigated by the interatomic pair potentials. In addition, the lattice vibrational properties for these rare earth compounds, each with a hexagonal Ce_2Ni_7-type structure, are evaluated with the relevant potentials for the first time.

2. Calculation method

The acquisition of interatomic potentials prepares the groundwork for this research. In the beginning of the 1980s, Carlsson *et al.* [17] reported that a pair potential could be obtained by *ab initio* cohesive energy curve, but the expression is indigestible for including infinite summations, each of which contains infinite terms. Different from the above method, Chen's lattice inversion formula based on *ab initio* cohesive energy[18,19] is a rigorous and concise technique to obtain interatomic pair potentials, which can concisely and uniformly express the inversion coefficient of ma-

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terials with identical structures, making its analysis convenient. In our previous work,[15,20] the methods for obtaining the potentials have been reported in detail. The inverted pair potentials from the cohesive energy are approximately expressed as Morse function

$$\Phi(x) = D_0(\mathrm{e}^{-\gamma(x/R_0-1)} - 2\,\mathrm{e}^{-(\gamma/2)(x/R_0-1)}),$$

where D_0, R_0, and γ are potential parameters. For the reader's convenience, several important potential parameters are shown in Fig. 1.

3. Calculation results

3.1. Structures of systems

The binary compound Nd_2Co_7 ($m = 2$, $n = 2$) is stable in the Nd–Co system and crystallizes into a hexagonal Ce_2Ni_7-type structure with the space group $P6_3/mmc$.[21−23] In a typical crystal cell with four Nd_2Co_7 molecular formulas (36 atoms per unit cell), there are five nonequivalent sites 2a, 4e, 4f (1/3, 2/3, 0.8338), 6h, 12k for Co atoms and two sites 4f (1/3, 2/3, 0.0268), 4f (1/3, 2/3, 0.1721) for Nd atoms. The values in brackets are the positions obtained from Ref. [21]. However, binary R_2Fe_7 does not exist, which is possibly due to a much higher mixing enthalpy between R and Fe than that between R and Co.[24] In order to study the effect of Fe atoms on the structural stability of a Nd_2Co_7 compound, we investigate theoretically the substitution behaviours of Fe in a $Nd_2Co_{7-x}Fe_x$ compound with a hexagonal structure. To avoid statistic fluctuation, a periodical super-cell $(Nd_2Co_{7-x}Fe_x)_{4\times4\times4}$ containing 2304 atoms is taken as a calculation unit. In the calculation, firstly, we substitute Fe atoms for Co atoms at each site with different concentrations. Then, the energy-minimization method is used to let the ternary system relax under the applied potentials. The average energy is taken as a criterion of the stability. The tolerance, which represents the displacement of the atomic position in order to retrieve the space group, is an auxiliary criterion. Numerical calculations show that when the tolerance is much larger than 0.5 Å, the compounds do not exist in experiment. In fact, the site occupation is determined by the energy and too large a tolerance means that the final stable structure deviates too far from the selected one and that the structure is changed.

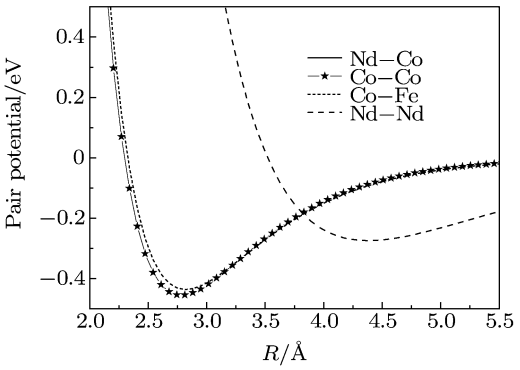


Fig. 1. Some important interatomic potentials.

Figure 2 shows that the calculated average energy and the tolerance of $Nd_2Co_{7-x}Fe_x$ each as a function of the Fe content x for the case of $x \leq 3.30$. The values of energy and tolerance in the figure are both statistically averaged over the calculations of 30 samples. Comparing these results, we find that the average energy decreases and the tolerance is acceptable for $x \leq 1.50$, illustrating that the introduction of Fe atoms may stabilize the crystal structure and that, correspondingly, the stabilized phases exist. Figure 2 clearly shows that the cohesive energy is lower when Fe atoms are substituted for Co atoms at the 6h site than at the 4e, 4f, 12k or 2a sites, and the tolerance is acceptable for $x \leq 1.50$. Fe should prefer the 6h site with the space group $P6_3/mmc$ for $x \leq 1.50$. As $1.50 < x < 2.50$, the energy of $Nd_2Co_{7-x}Fe_x$ is calculated on the assumption that Fe has occupied all the 6h sites. In that case, the energy for an Fe atom entering into the 4e site is the lowest and the tolerance is acceptable for $1.50 < x < 2.50$. Therefore, in the calculation, when $0 < x \leq 1.50$, an Fe atom prefer to stay at the 6h site. When $1.50 < x < 2.50$, Fe atoms should first occupy all of the 6h sites, and then with 6h being full, Fe atoms should enter into part of the 4e sites. The order of site preference is 6h, 4e, 4f, 2a, and 12k. It is found in Fig. 2 that the cohesive energy of $Nd_2Co_{7-x}Fe_x$ increases with the increase of the Fe content for $x > 2.50$ and the tolerance is so large that a $Nd_2Co_{7-x}Fe_x$ compound with a structure of Ce_2Ni_7-type could not be stable. The result is almost consistent with that of the $Nd_2Co_{7-x}Fe_x$ compound in the experimental report.[21] When $x = 2.50$, the energy of the 4e sites rapidly rises and the tolerance suddenly drops down to 0.01 Å. This is because the Fe atoms at the particular sites are all substituted and the structure of the system is very symmetrical. The energy dependence curve as a function of Fe is concave for $x > 1.50$. By inference, the structure of

$Nd_2Co_{7-x}Fe_x$ becomes more and more unstable as x increases, so the stable phase Nd_2Fe_7 is not expected to appear according to this calculation (Fig. 2). This indicates that the Nd_2Co_7 structure is much more stable than the Nd_2Fe_7 structure, which is just as the R_2T_7 series reported in Ref. [24].

With the same potential, we also calculate the equilibrium lattice constants of the $Nd_2Co_{7-x}Fe_x$ compounds. The calculated results are listed in Table 1 together with the experimental data from Ref. [21]. We notice that the largest deviation of the calculated equilibrium lattice constant a is 2.33 % from the experimental value, while that of c is 0.70 %. In our calculation, it is assumed that $Nd_2Co_{7-x}Fe_x$ has a relatively perfect periodic crystal structure, Fe atoms occupy the 6h sites for $x < 1.50$, and six Fe atoms are entirely distributed over the 6h sites for $x > 1.5$. These assumptions may result in a deviation of the calculations from the experimental data.

In the above calculations, the effect of temperature on the crystal structure is not considered. During the simulation, the constant-NPT ensemble is used, and the extended system with a thermostat and barostat relaxation time of 0.10 ps is adopted. The temperature range for the simulation is 100 K–900 K with a step of 200 K. For each temperature and at 1 atm pressure, calculations are performed for 30000 steps with a time step of 2.0×10^{-15} s. After reaching equilibrium, the $Nd_2Co_{7-x}Fe_x$ compound with a hexagonal structure is stable. Lattice constants are found to change very little with respect to the temperature variation.

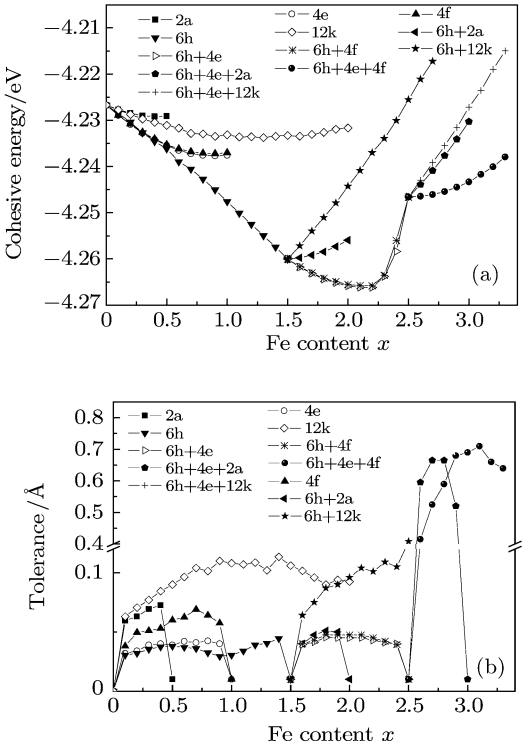


Fig. 2. Calculated (a) cohesive energies and (b) tolerances of $Nd_2Co_{7-x}Fe_x$.

Table 1. Structural parameters a and c for $Nd_2Co_{7-x}Fe_x$.

x	a/Å			c/Å		
	Cal.	Exp.	Err./%	Cal.	Exp.	Err./%
0	5.1830	5.0648	2.33	24.6355	24.4652	0.70
0.2	5.1828			24.6211		
0.4	5.1821	5.0702	2.21	24.6045	24.4413	0.67
0.5	5.1818			24.5959		
0.8	5.1802	5.0809	1.95	24.5839	24.4233	0.66
1.0	5.1800	5.0898	1.77	24.5709	24.4517	0.49
1.5	5.1775	5.1010	1.50	24.5485	24.4486	0.41
1.8	5.1773	5.1063	1.39	24.5365	24.4307	0.43
2.0	5.1767			24.5299		
2.4	5.1765	5.1155	1.19	24.5225	24.4308	0.38

3.2. Interatomic distance and Curie temperature of $Nd_2Co_{7-x}Fe_x$

From Ref. [21], the Curie temperature T_C increases obviously with the increase of Fe concentration in $Nd_2Co_{7-x}Fe_x$ compounds. In order to study the variation trend of the Curie temperature, the distance between special sites and the relevant exchange interaction in the $Nd_2Co_{7-x}Fe_x$ compound are calcu-

lated. In the R–T compound, there are three kinds of exchange interactions, the R–R, the T–T, and the R–T interactions. Among them the T–T interaction is the strongest one and the R–R interaction is the weakest. Since the Co–Co exchange-coupling constants are about one order of magnitude larger than the R–Co exchange-coupling constants, the Curie temperature in Co-rich rare earth-cobalt intermetallics is determined mainly by the Co–Co exchange interaction.

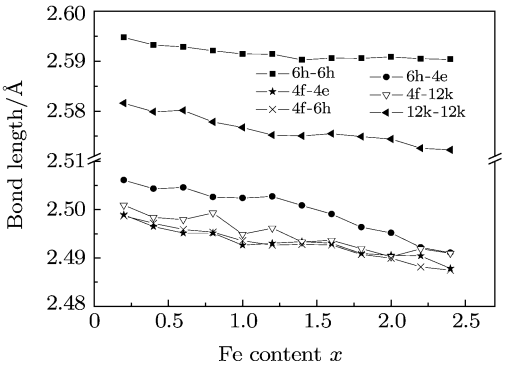


Fig. 3. Bond length of Co–Co with Fe content in $Nd_2Co_{7-x}Fe_x$.

Figure 3 shows the bond lengths of Co–Co pairs in $Nd_2Co_{7-x}Fe_x$, indicating that the length decreases with Fe content increasing in $Nd_2Co_{17-x}Fe_x$. When Fe atoms are substituted for Co atoms, the decrease of the Co–Co inter-atomic distance leads to an increase of the Co–Co exchange interaction, which will increase the Curie temperature.

3.3. Lattice vibration of $Nd_2Co_{7-x}Fe_x$

In this subsection, we calculate the total phonon density of states (DOS) and the partial DOSs of different elements for $Nd_2Co_{7-x}Fe_x$ (x = 0.5, 1.0, 1.5, 2.0) in a crystal cell including 36 atoms. Figure 4 shows the results considering the contribution to the DOS of the distinct atoms. It can be seen from the total DOS that the highest frequencies of intermetallics $Nd_2Co_{7-x}Fe_x$ (x = 0.5, 1.0, 1.5, 2.0) are 9.54, 9.42, 9.38, and 9.03 THz, respectively. For each spectrum, it can be divided into two parts at about 7.56, 7.59, 7.58, and 7.41 THz, respectively, where the phonon density is almost zero. The second part is called the high frequency localized mode. The Nd atoms contribute a major part to the modes with lower frequencies. The vibrational modes are mostly excited by Co atoms in the total frequency and high frequency localized modes. The contribution of the ternary element Fe to frequency modes is similar to that of Co, but the intensity of the mode of Fe is much smaller. The spectrum peaks of Fe atoms are enhanced as x increases.

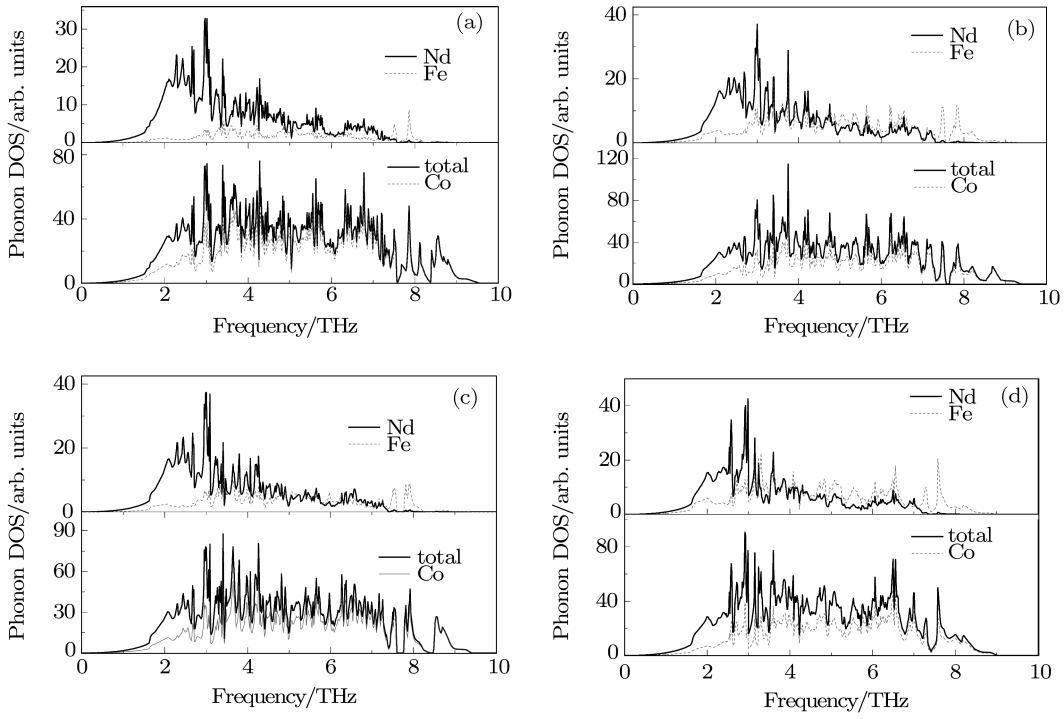


Fig. 4. Phonon densities of states of $Nd_2Co_{7-x}Fe_x$: (a) $Nd_2Co_{6.5}Fe_{0.5}$, (b) $Nd_2Co_6Fe_1$, (c) $Nd_2Co_{5.5}Fe_{1.5}$, (d) $Nd_2Co_5Fe_2$.

We utilize inverted interatomic potentials to qualitatively analyse the modes by considering only the nearest neighbours. We can choose $x = 1.5$ in a $Nd_2Co_{7-x}Fe_x$ system for an example. There are four Co atoms at the 12k sites, three Co atoms at the 2a sites and three Co atoms at the 12k sites around Nd. The distances between Nd and these atoms are 2.93, 3.02, and 3.17 Å, respectively. As shown in Fig. 1, the potentials change steeply at these distances, which means that Nd atoms react strongly with Co atoms at these distances. The mass of a Nd atom is much larger than that of a Co atom, so the Nd atom is assumed to be motionless relative to the Co atom. Then some Co atoms are restricted in the potential well $\Phi_{\mathrm{Nd-Co}}(r)$. This might be the reason for the occurrence of the localized modes of Co atoms, which corresponds to a higher transverse frequency. Nd atoms contribute only to lower frequency vibrations in the Nd–Co potential well because of their large atomic mass. In addition, the very strong interaction (see Fig. 1) between Co atoms at their nearest distance (2.49 Å) causes Co to vibrate at a total frequency. From Fig. 1, it can be seen that the potential interaction of Co–Co is nearly the same as that of Co–Fe. Hence, the frequency modes of Fe atoms are almost the same as those of Co atoms in shape, but the amplitudes are much smaller because the number of Fe atoms is small.

Furthermore, the specific heat, vibrational entropy and Debye temperature can be obtained by the calculated phonon DOS. Figure 5 gives the calculated lattice specific heat and vibrational entropy of $Nd_2Co_{7-x}Fe_x$ as a function of temperature. The results show that the values of the specific heat and the vibrational entropy increase with the Fe content increasing. The Debye temperature of a material is a suitable parameter for describing the properties of the material at a lower temperature and lower frequency. Figure 5 also shows the variations of the Debye temperature for $Nd_2Co_{7-x}Fe_x$ ($x = 0.5$, 1.0, 1.5, 2.0) with the temperature increasing from 0 to 200 K. Their values are 364, 362, 360, and 348 K at near 0 K, respectively. Apparently, the Debye temperature decreases as the Fe content increases. Therefore, Fe may play an important role in the lower-temperature properties of these materials. As a last point, because the experimental results are unavailable, we cannot compare our results on DOS. This makes it possible to predict some properties related to lattice vibration.

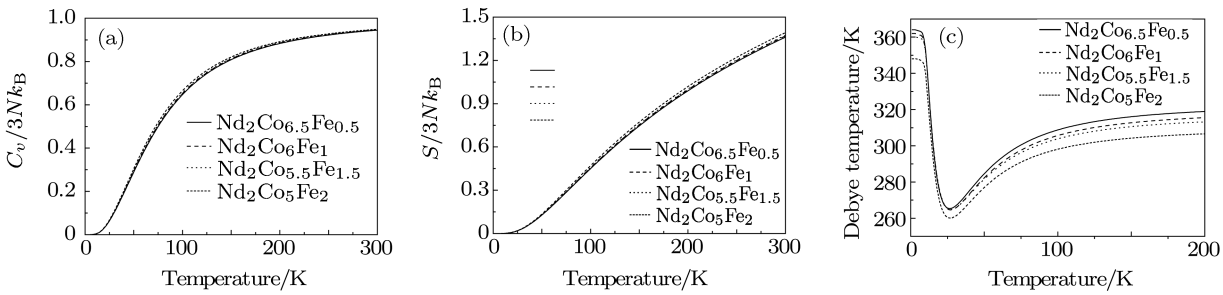


Fig. 5. Calculated values of (a) specific heat, (b) vibrational entropy and (c) Debye temperature of $Nd_2Co_{7-x}Fe_x$ (N represents the number of atoms in each cell).

4. Conclusion

Inverted potentials based on *ab initio* calculations and the lattice-inversion method are used to calculate the phase stabilities, lattice parameters and site preferences of the $Nd_2Co_{7-x}Fe_x$ compounds. It is found that the Fe atoms prefer to occupy the 6h sites and the order of site preference is 6h, 4e, 4f, 2a, and 12k. The calculated lattice constants are found to be accordant with the results reported in the literature. Furthermore, we utilize the same potential parameters to evaluate the vibrational properties of rare earth compounds. The computational investigation from the viewpoint of energy also features in dealing with rare earth materials. Encouraged by the previous work on $U_6Fe_{16}Si_7$ [25] and the work on $A_4Fe_3Al_{32}$ [26] here, we are confident in future work on actinide and rare earth material structure research and prediction. Finally, it should be mentioned that the current work does not include many-body interaction and magnetic effects, which might be the next objective of our work.

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