First-Principles Study on Electronic Structures of Rich-Ni Al-based Quasicrystals Cluster

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Abstract. The geometrical structure, electronic properties, surface energy and formation enthalpy of Ni-rich Al-based quasicrystals cluster models have been studied with the generalized gradient approximation (GGA) based on the density functional theory (DFT). Based on the first-principles calculation method, the ground state structures of 5f and 10f clusters are changed obviously due to atomic position space occupy around cluster center and their symmetry. The results from calculation demonstrate that the 10f model has smaller energy gap.

1. Introduction

Since the discovery of quasicrystalline I-phase in Al-Mn alloys, two dimensional quasicrystal phase aslo was investigated in Al-Co-Ni alloy [1]. For unit cell of Al-Co-Ni quasicrystal, the diameter of 10-fold and 5-fold symmetric pentagonal columnar clusters are 2 nm, for basic Ni-rich structure the gap of layer is 0.2 nm. There exists short-range chemical order inside clusters, which means the first-principles calculation could be employed to study its structural properties [2,3,4].

The physical and chemical properties of quasicrystal have been studied in experiments by scholars, but the electronic properties of quasicrystals are rarely considered [5]. Especially for thermally stable Al-Ni-Co quasicrystal system, first-principles calculations can provide important insights to the understanding of quasi-periodic clusters [6,7].

In this paper, the structure, energy, geometry optimization, electronic density of two dimensional Al-Ni-Co quasicrystals were investigated. There were two cluster models of this quasicrystal, one is 5-fold symmetry (5f) cluster and the other is 10-fold symmetry (10f) cluster. By comparing the energy of the two models, we found Ni-rich 10f cluster model were more stable. The displacement of the ten atoms in the center implied the position change caused by thermodynamic conditions. The electron density shows an internal perspective to explore the particular physical and chemical properties of Al-Ni-Co quasicrystals.

2. Models and Calculations

In this study, there are two models which are Ni-rich 10f and Ni-rich 5f models, they both have two layers as showed in Fig. 1, while the distance of the two layers is 0.2 nm, and the diameter of a columnar cluster is 2 nm. Hypothetical lattice constants are $a = b = 3$ nm, $c = 1.2$ nm, $\alpha = \beta = \gamma = 90$, which could assure that calculations of the cluster would not be affected by their nearby clusters. For Ni-rich Al-Co-Ni quasicrystal, Ni-potential was employed to simplify the calculations. The chemical composition of both Ni-rich 10f and Ni-rich 5f models are $Al_{55}Ni_{35}$. The orange atoms are Al, while the other blue ones are Ni.

The CASTEP [8], based on the first principles density functional theory, within the GGA was used to perform the calculations. For the GGA exchange-correlation, the Perdew-Burke-Ernzerhof [9] was employed.

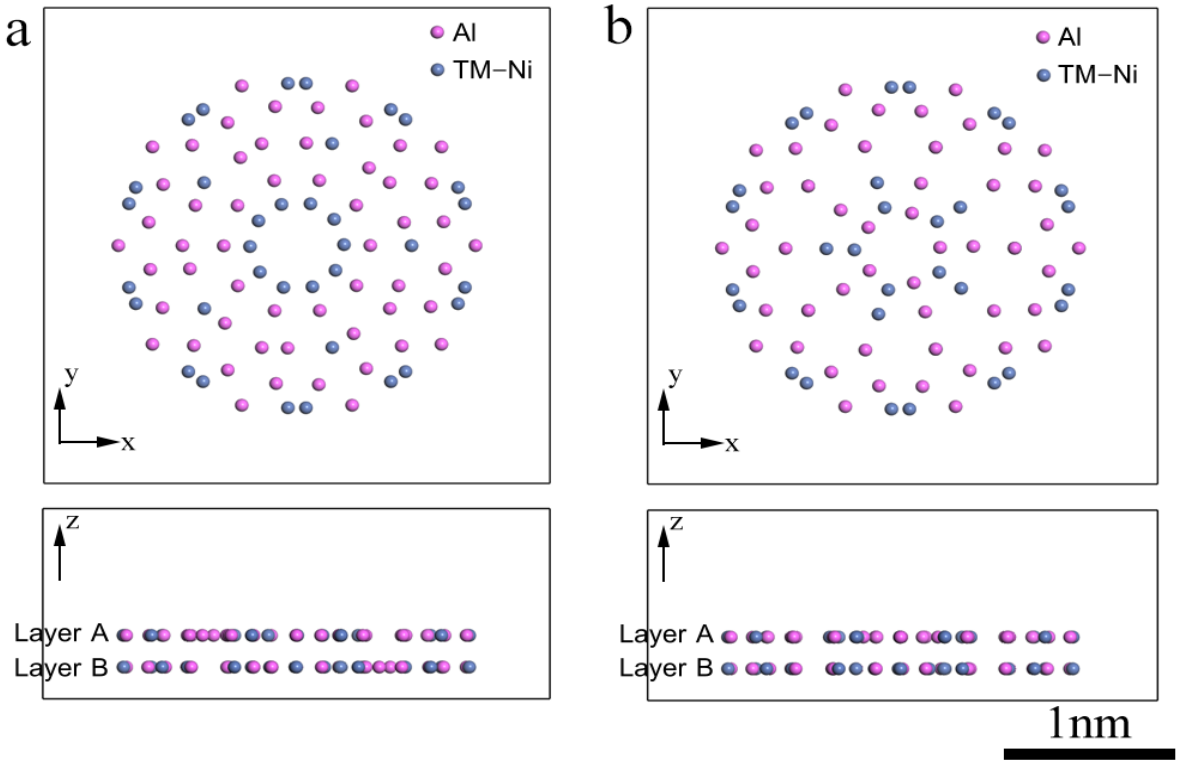

Fig. 1. Atomic cluster models of Ni-rich 10f (a) and Ni-rich 5f (b)

Ultrasoft pseudo-potential and plane wave basis sets were applied [10]. The cutoff energy was tested from 300eV to 500eV, but the difference of ground state energy was less than 0.1‰. So the cutoff energy was set at 300eV to improve efficiency. The *k*-points were tested from 1×1×1 to 1×1×3, the difference of the ground state energy was also less than 0.1‰, so the *k*-points were set at 1×1×1. And the self-consistent convergence of the total energy was lower than 1×10^{-6} eV/atom. The geometry optimization was used the BFGS method. Forces on atoms were calculated through the Hellmann-Feynman theory as the partial derivatives of the free energy with respect to the atomic position. And the force was smaler than 0.03eV/Å.

3. Results and Discussion

3.1 Geometry Optimization

According to four layers $Al_{110}Ni_{70}$ model (ABA'B') calculation results, when all atoms of 5f and 10f models were constrained except the center ten atoms in the layer B and A', it was found that some displacement of the ten atoms seemed to be consistent with the thermal motion.

Table 1 Position changes of central atoms in Ni-rich 10f model after geometry optimization. (Å)

Coordinates / Atoms	*x*	*y*	*z*	*x'*	*y'*	*z'*	*d*
Ni1	12.720	16.560	4.000	12.604	16.672	4.085	0.182
Ni2	15.801	17.637	4.000	15.835	17.672	4.065	0.081
Ni3	17.790	15.060	4.000	17.830	15.025	4.037	0.064
Ni4	15.918	12.405	4.000	15.943	12.263	4.074	0.162
Ni5	12.801	13.332	4.000	12.658	13.243	4.092	0.192
Ni6	17.286	13.440	2.000	17.300	13.362	1.968	0.086
Ni7	14.202	12.360	2.000	14.162	12.346	1.992	0.043
Ni8	12.216	14.940	2.000	12.195	14.960	1.996	0.030
Ni9	14.085	17.595	2.000	14.087	17.633	1.992	0.039
Ni10	17.205	16.659	2.000	17.269	16.692	1.965	0.080

Specific changes has taken place in the geometry optimization which were shown as Table 1 and Table 2, it should be noted that the displacement (*d*) are less than 0.2 Å, this phenomenon was similar to the experinental thermal motion of Al-Ni-Co quasicrystals.

Table 2 Position changes of central atoms in Ni-rich 5f model after geometry optimization. (Å)

Coordinates / Atoms	*x*	*y*	*z*	*x'*	*y'*	*z'*	*d*
Al1	12.981	16.178	4.000	12.924	16.200	4.063	0.088
Al2	13.049	13.464	4.000	13.015	13.421	4.062	0.083
Al3	15.656	12.688	4.000	15.684	12.647	4.062	0.079
Al4	17.202	14.919	4.000	17.256	14.939	4.063	0.085
Al5	15.547	17.078	4.000	15.545	17.131	4.062	0.082
Ni1	12.161	14.766	2.000	12.221	14.799	2.066	0.095
Ni2	14.151	12.246	2.000	14.129	12.320	2.066	0.102
Ni3	17.153	13.354	2.000	17.080	13.365	2.069	0.101
Ni4	17.029	16.546	2.000	16.995	16.481	2.066	0.099
Ni5	13.943	17.425	2.000	13.989	17.368	2.067	0.099

After relax, in 10f model, the center atoms of layer B and A' are moving closer to layer A and B', with u_B = 0.071 Å and $u_{A'}$ = -0.018 Å. In the 5f model, after relax, the five Al atoms of layer B are closer to layer A (u_B = 0.062 Å), and the layer A' five Ni atoms are moving far away from layer B' ($u_{A'}$ = 0.067 Å). It implies that higher temperature variation lead to a active displacement in the center of quasicrsytal clusters.

3.2 Ground State Energy

The bulk stability of the compound is determined by formation enthalpy. The negative formation enthalpy change means the structure is thermodynamically stable and the positive value implies the structure is instable [11]. The bulk energy is calculated by using the following expression:

$$E_{bulk} = (E_a - E_b)/(a-b) \quad (1)$$

Where E_a is the ground state energy of four-layer quasicrystal, and E_b is the ground state energy of two layers. By Eq. 1, the ground state energy of single layer, which is the bulk energy, can be calculated. With the bulk energy, the surface energy is calculated as following expression [12]:

$$E_{surf} = (E_{slab} - n \cdot E_{bulk})/2A \quad (2)$$

A is the area of the columnar clusters' top surface, E_{slab} is total energy of a slab with n layers. After solving Eq. 2, the formation energy is defined as:

$$\Delta H_f = [(2E_{bulk} - \sum(n_i \cdot E_i)]/\mathrm{n} \quad (3)$$

E_i is the energy per atom of bulk system, n_i represent the number of the reference atom in the layers. n is the total number of the atoms. The formation enthalpy is summarized in table 3 by Eq. 3. The results of ΔH_f are negative and clearly verify the stability of the studied compounds.

Table 3 Calculated ground state energies (eV/atom), surface energy (eV/nm^2) and formation enthalpy (eV/atom)

Symmetry	*E* (eV/atom)	E_{surf} (eV/nm^2)	ΔH_f (eV/atom)
10f	-541.986	10.762	-4.770
5f	-541.809	10.318	-4.563

3.3 Electron Density

Electron density has been calculated to study the nature of the bonds. Fig. 2(a)-(c) are layer A and B of Ni-rich 10f model, Fig. 2(b)-(d) are layer A and B of 5f model. Black contrast distribution represents higher charge density while gray areas represents lower.

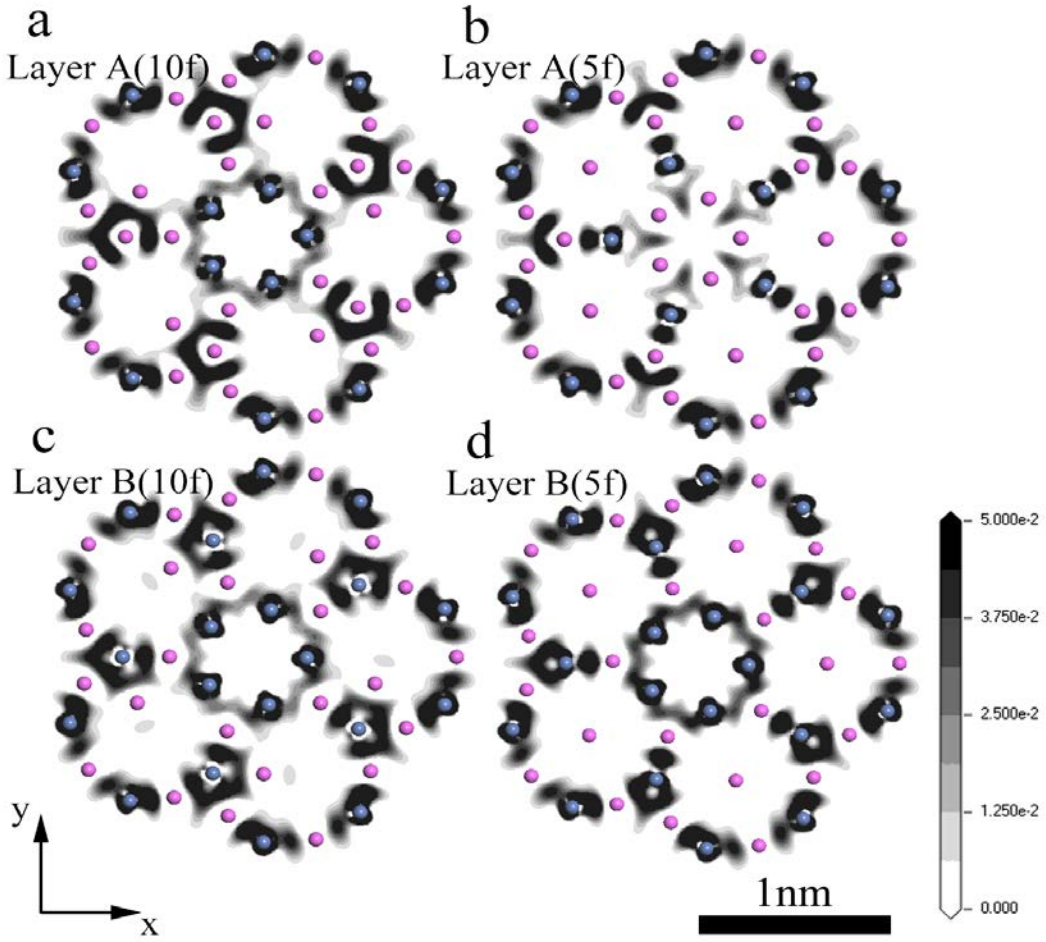

Fig. 2. Electron density of layer A and layer B of Ni-rich 10f (a,c) and Ni-rich 5f (b,d) models

Partial enlarged images of electron density maps of Ni-rich quasicrystal model are shown as Fig. 3 and Fig. 4, which clearly indicates the cluster central electronic compositions of band structures.

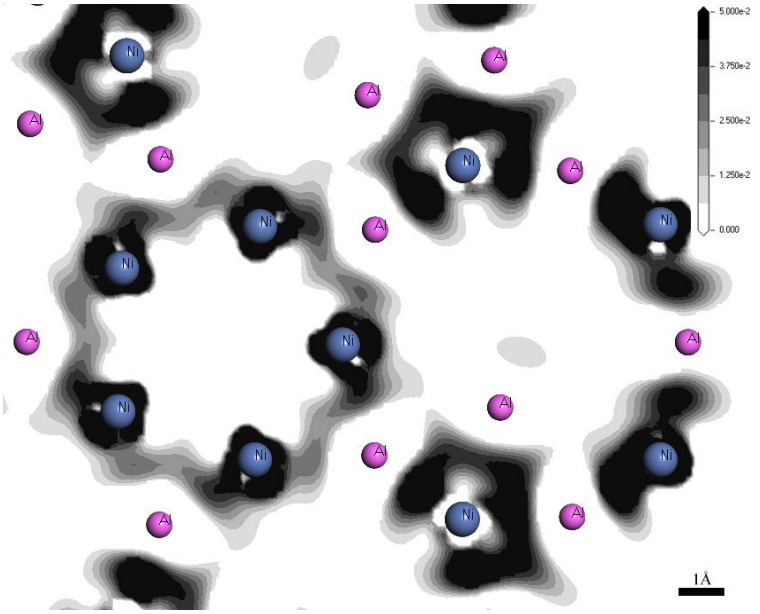

Fig. 3. Partial electron density of layer B of Ni-rich 10f model

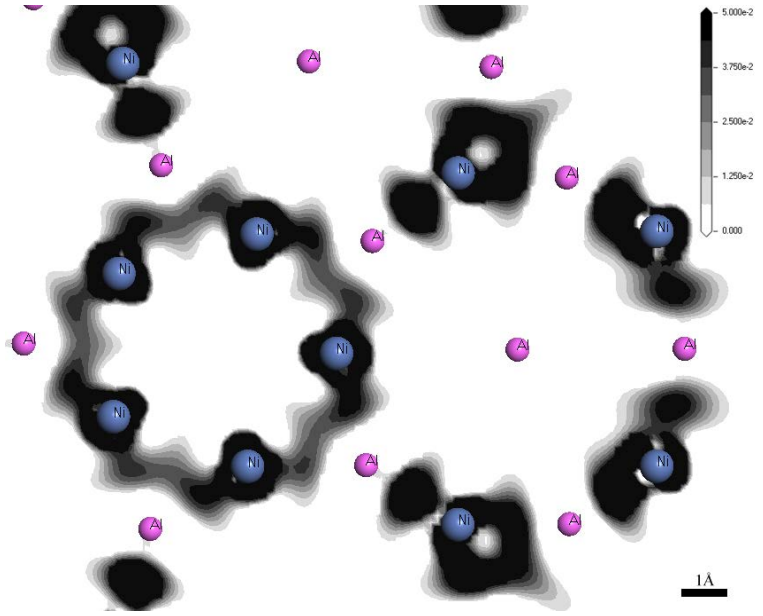

Fig. 4. Partial electron density of layer B of Ni-rich 5f model

In general, with higher value of electronegativity 1.88, the Ni atom have more powerful ability to attract electrons from near Al atoms (electronegativity is 1.61). So, there are higher density of electron clouds around Ni atoms. in Fig. 4, the electron clouds around the central five Ni atoms is different, while same area have deeper electron density contrast in Fig. 4. The differece means the tighter combination of central five Ni atoms, which probably leads to low coherence with nearby Al atoms, then the stability of model is worse, just as shown in the energy analysis.

Summary

We performed first principles calculations to investigate the geometrical structure and electronic structures of Ni-rich 5f and 10f Al-based quascrystal cluster models. The surface energy and formation enthalpy was also calculated to establish linkage between the local chemical ordering and atomic displacement.

Acknowledgements

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