

AlTiNi Ternary Alloy Clusters: Molecular Dynamics Simulations and Density Functional Theory Calculations

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Structural and electronic properties of $\text{Al}_k\text{Ti}_l\text{Ni}_m$ ($k + l + m = 4$) clusters have been investigated by performing molecular dynamics (MD) simulations and density functional theory (DFT) calculations (within the B3LYP and effective core potential level). After an empirical potential energy function (PEF) was parametrized for the AlTiNi ternary system, stable structures of the clusters were determined by MD simulations. The possible dissociation channels and electronic properties of the obtained clusters were calculated by the DFT method. The energetics of the clusters at 1 and 300 K are also discussed.

Introduction

The cluster area has been one of the most actively studied research fields since 1980s. The literature of the past two decades is full of numerous theoretical and experimental studies devoted to explore the structural and electronic properties of small atomic and molecular clusters. The results of these studies and their applications have been collected in several reviews^{1–7} and books.^{8–22} The far-reaching consequences of these studies and their practical and possible industrial applications have made the cluster area an interdisciplinary place in the intersection point of quantum chemistry, solid-state physics, surface science, atomic and molecular physics, etc. Among the studies of clusters are abundances, catalysis, chemisorption and substrate adsorption, crystal growth, electronic structures, equilibrium structures, evolution of surface properties, laser applications, magic numbers, magnetism, nanostructures, nucleation, photographic processes, reactivity, and properties as a function of cluster size.^{1–22}

Clusters are generally defined as small aggregates of atoms. Their sizes are intermediate between constituent atoms and bulk matter. The number of atoms, N , making up a cluster is no more than a few hundred or at most a thousand; beyond this enters the field of nanoscale materials. *Small* clusters have structural and electronic properties which depend strictly on N . It is hardly possible to correlate these properties with smoothly varying functions of N . The properties of a *large* cluster usually approach those of the corresponding bulk material. This puts the large clusters in front of the main door to the realm of the solid state. Consequently, clusters can be thought to be on the border separating molecules from liquids and solids and this fact is perhaps the most important reason for the indispensability of the cluster area. From atoms and molecules to liquids and solids, it is possible only with the help of the studies of clusters to understand the evolution of structural and electronic properties of the solid state.^{16,17,23} (For a good discussion, the reader is recommended to look also at ref 24, where clusters are described to be in the “mesoscopic” region between the microscopic region of atoms or molecules and the macroscopic region of the condensed matter. In that review, the authors build a bridge,

for this mesoscopic region of clusters, between microscopic and macroscopic regions. They discuss *analytic cluster models* enabling simple interpolation formulas for the size dependence of various stationary cluster properties. The verification of the given interpolation formulas for electronic, geometrical, kinetic, optical, electrical, and magnetic properties is presented. They show how beautifully the cluster properties approach those of bulk.)

In the literature, the transition-metal (TM) clusters have drawn intense interest because of their physical, chemical, and obvious economical importance. (References 1–3 present the experimental data and theoretical results concerning TM clusters.) Their widespread use in the studies of catalysis processes, chemisorption and substrate adsorption, nucleation, photographic processes, and possible laser applications make the chemistry of TMs a hot research area. All these reasons render the studying of the properties of TM clusters profitable.

The present study is the continuation of our previous work²⁵ (which includes a detailed reference list about the studies of clusters) where we investigated the structural and electronic properties of $\text{Al}_k\text{Ti}_l\text{Ni}_m$ ($k + l + m = 2, 3$) clusters by performing density functional theory (DFT) calculations. The clusters of aluminum, nickel, and titanium are again the subject of this paper, but this time $k + l + m = 4$. From the metallurgical point of view, their binary and ternary alloy systems have become popular recently. Their crystal structure, phase diagram data, electronic structure, optical properties, etc. have been investigated intensely.^{26–34} This intense interest in these elements is due partly to their shape-memory-alloy properties that make them industrially important.^{35,36} Our interest in AlTiNi ternary clusters is to determine the very basic building blocks of and to explore the clustering phenomenon in these economically promising alloy systems. We desire to investigate systematically the simpler potential candidates for the building blocks, namely Al_2 , Ti_2 , Ni_2 , AlTi, AlNi, TiNi, Al_3 , Ti_3 , Ni_3 , Al_2Ti , Al_2Ni , AlNi_2 , Ti_2Ni , TiNi_2 , as we did in our previous study,²⁵ and the more involved candidates Al_4 , Ti_4 , Ni_4 , Al_3Ti , Al_2Ti_2 , AlTi_3 , Al_3Ni , Al_2Ni_2 , AlNi_3 , Ti_3Ni , Ti_2Ni_2 , TiNi_3 , Al_2TiNi , AlTi_2Ni , AlTiNi_2 , the subject of this study. Our general objective is to get a general understanding of geometrical and electronic properties about these clusters, which is believed to lead to valuable insights into the evolution from small clusters

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to the bulk AlTiNi ternary alloy system. In this regard, we propose to continue our research series toward the larger clusters of the AlTiNi system. In this study, structural and electronic properties of the 15 different clusters listed above have been investigated theoretically in their ground states. This work is composed of two stages. In the first stage, we have parametrized a reliable empirical potential energy function (PEF) for the AlTiNi ternary system. The PEF used in the calculations includes two- and three-body atomic interactions which were respectively represented by Lennard-Jones- and Axilrod-Teller-type functions. Then, performing molecular dynamics (MD) simulations, we obtained and reported minimum energy configurations for the clusters. A discussion about the energetics of the species at both 1 and 300 K then follows. We compared the energetically most stable geometries with the previously reported ones computed by various other approximate methods and estimated experimentally (available only for Al₄ and Ni₄). In the second stage, to explore the electronic properties of the most stable clusters obtained from MD simulations, we have performed the density functional theory (DFT) calculations within the effective core potential (ECP) level with the B3LYP exchange-correlation potential. The DFT calculations were carried out by using the GAUSSIAN 98 package.³⁷ For all the clusters considered, the possible dissociation channels and the corresponding dissociation energies, the calculated highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and HOMO-LUMO gap energies are presented. The calculated dipole moments and excess charges on the atoms of the four-atom clusters are also given.

Methods of Calculations

Empirical Many-Body PEF. Making use of computer simulations, empirical many-body PEFs have been successfully used to investigate various properties of bulk, surface, and clusters of elements at the atomistic level. A PEF is a parametric function designated to describe the interactions among the atoms in a system. It is parametrized to give the empirical data for the system under consideration. Apart from the condition that a PEF must possess all physically required invariance properties, it is usually desired to have a small number of parameters because the more parameters a PEF has, the more time-consuming the parametrization becomes.

Assuming that, in the absence of external forces, there exists a PEF, $\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, to describe the total potential energy of a system of N atoms as a function of their positions, it can be expanded into the contributions from two-body, three-body, ... interactions,³⁸ like the multipole expansion in electrostatics:

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i < j} U_{ij}(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i < j < k} W_{ijk}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots \quad (1)$$

Believing that this series is rapidly convergent and that the first two terms, the two- and three-body contributions, suffice for a reasonable approximation to the total potential energy, the higher moments of the PEF are usually neglected.^{39,40} In the early applications, only the two-body term has been taken into account. It has been shown later, however, that the three-body term was essential in the structure and the stability concerns of different clusters.⁴¹

In this study, expansion 1 has also been truncated after the second term so that only the two- and three-body interactions were included. The Lennard-Jones potential has been taken for the two-body part, and the Axilrod-Teller triple-dipole potential for the three-body part,⁴² their explicit forms respectively are

$$U_{ij} = \epsilon_0 \left[\left(\frac{r_0}{r_{ij}} \right)^{12} - 2 \left(\frac{r_0}{r_{ij}} \right)^6 \right] \quad (2)$$

and

$$W_{ijk} = \frac{Z(1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k)}{(r_{ij} r_{ik} r_{jk})^3}, \quad (3)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the interatomic distance between atoms i and j ; r_0 is the equilibrium distance of the pair potential, where the pair energy assumes its minimum value, ϵ_0 ; θ_i , θ_j , and θ_k are the angles of the triangle formed by the three atoms i , j , k ; and Z is the three-body (intensity) parameter. Maybe we should emphasize here that, in the literature, this empirical many-body potential energy function, eq 1 with eqs 2 and 3, is the one that has the least number of parameters for a monatomic system, namely r_0 , ϵ_0 , and Z .

MD Simulations Technique. In this work the equations of motion for the AlTiNi ternary system have been solved employing a MD technique based on the Nordsieck-Gear algorithm,^{43,44} through the seventh-order predictor–corrector method.⁴⁵ For each cluster calculation 20 000 time steps (each time step was 1.5×10^{-15} s) were enough to reach thermal equilibrium at 1 K. Temperature rescaling was maintained during the whole simulation. Thermal equilibrium was controlled by checking the time-averaged energy after each 100 steps. The statistical averages are also checked after every 500 steps.

DFT Method. Since the present study is the continuation of our recent work²⁵ and it has somewhat detailed information about the DFT method, it should be sufficient here to give only a brief description about the method. In this work, to explore their electronic structure properties, Al_kTi_lNi_m ($k + l + m = 4$) clusters, obtained as having most stable structure from the MD simulations (see below), have been investigated theoretically by performing density functional theory calculations.⁴⁶ The exchange and correlation potential contributions have been considered at the B3LYP level.⁴⁷ The compact effective potential (CEP) basis functions with ECP triple-split basis, namely CEP-121G,^{48–50} have been used in the calculations. The DFT calculations were performed by using the GAUSSIAN 98 package.³⁷

Results and Discussions

Parametrization of PEF. Making use of the available experimental data and the quantum mechanical calculation results for dimers and trimers of Al, Ni, and Ti (see Tables I–III and V in ref 25; we have not taken Table IV into account because there was no available experimental data for the heteronuclear dimers of the elements under consideration), we have determined the parameters, (r_0 , ϵ_0 , Z) of the PEF, eqs 1–3, for the AlTiNi ternary system. The binding energy (i.e. pair energy) and the interatomic equilibrium distance for two-atom clusters, as well as the binding energy (i.e. formation energy) and the geometry for three-atom clusters, have been taken into account during the parametrization process. The main objective was to re-obtain the geometry and the total energies of the dimers and trimers of the elements under consideration as close as those resulting from experiments and, at the same time, those resulting from the previous ab initio results. The thus-obtained parameter set for the AlTiNi ternary system is presented in Table 1. We should point out here that this parameter set can be more suitable for cluster applications; it is, not surprisingly, likely that it might not properly work for bulk properties. This is due

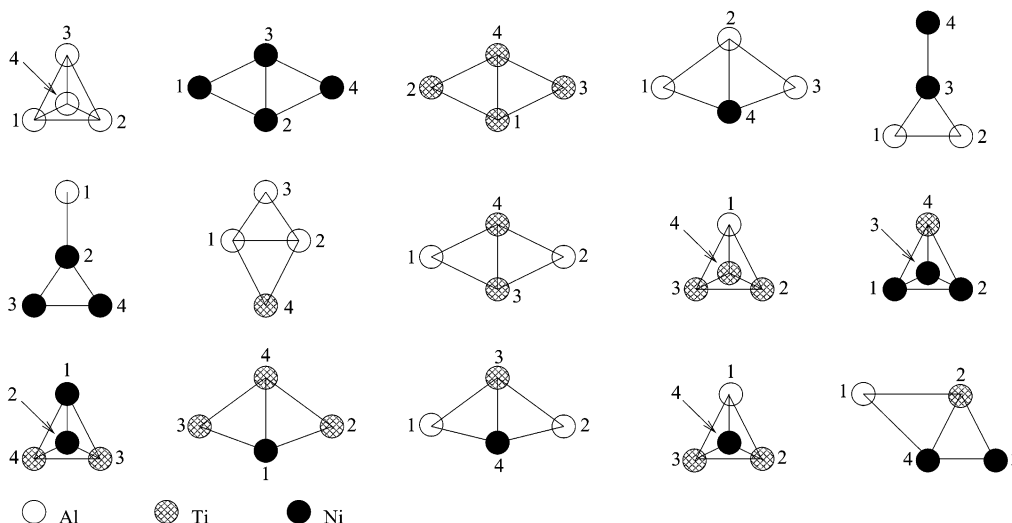


Figure 1. Structures of clusters optimized with use of the empirical potential via MD simulations.

TABLE 1. Empirical Potential Energy Function Parameters Determined for the Al–Ti–Ni Ternary System

two-body parameters			three-body parameters	
dimer	ϵ_o (eV)	r_o (Å)	trimer	Z (eV Å ⁹)
Al ₂	1.60	2.55	Al ₃	3000.0
Ti ₂	2.00	2.30	Ti ₃	1760.0
Ni ₂	2.20	2.22	Ni ₃	1813.0
AlTi	1.70	2.70	Al ₂ Ti	6000.0
AlNi	1.70	2.25	AlTi ₂	500.0
TiNi	2.20	2.00	Al ₂ Ni	1510.0
			AlNi ₂	3810.0
			Ti ₂ Ni	600.0
			TiNi ₂	250.0
			AlTiNi	290.0

to the fact that we have not made use of bulk properties in the parametrization procedure, instead we have used only the two- and three-atom properties mentioned above.

The mentioned parametrization procedure is not like the least-squares fitting method; it is merely a numerical search aimed at obtaining the predetermined geometry and energy of the system studied. We first reasonably fixed two of the three parameters (i.e., r_o , ϵ_o , Z) by making use of the experimental and ab initio results and allowed the third one to vary until we obtained a structure that had a geometry and energy close to the predetermined ones. We repeated this process for each of the three parameters until we got the optimum result possible.

MD Simulations Results. Having fixed the empirical potential parameters, we have used the new potential in the simulations of four-atom clusters of the elements under consideration, $Al_kTi_lNi_m$ ($k + l + m = 4$), by MD technique. Since clusters assume their geometry according to the local minima on the potential energy surface (PES) of the system, a cluster should be expected to have as many “isomers” as the number of local minima, just like molecules. To “catch” the real minimum energy configuration of the system, corresponding to the global minimum on the PES, one then must try as many initial configurations as possible at low temperature. Although the difference in the interaction energy of the isomers is usually small, their structures may be greatly different. (Here an important point is in order: there exist some well-known standard methods to determine the global minimum-energy configuration of a system. For example, a single initial configuration can be optimized either through the simulated annealing or quenching, or through the conjugated gradient and steepest descent methods. There should be no doubt that it is more likely

TABLE 2. Interatomic Distances (in Å) of the Stable Clusters Obtained as the Result of MD Simulations^a

cluster	dimensionality	d_{12}	d_{13}	d_{14}	d_{23}	d_{24}	d_{34}
Al ₄	3D	2.67	2.67	2.67	2.67	2.67	2.67
Ti ₄	2D	2.36	2.36	2.46	4.02	2.35	2.35
Ni ₄	2D	2.29	2.29	3.88	2.43	2.29	2.29
Al ₃ Ti	2D	2.71	2.60	2.78	2.60	2.78	4.64
Al ₂ Ti ₂	2D	4.88	2.70	2.70	2.70	2.70	2.31
AlTi ₃	3D	2.72	2.72	2.72	2.37	2.37	2.37
Al ₃ Ni	2D	2.63	4.25	2.28	2.63	2.35	2.28
Al ₂ Ni ₂	2D	2.61	2.25	4.20	2.25	4.21	2.16
AlNi ₃	2D	2.18	4.27	4.28	2.26	2.26	2.30
Ti ₃ Ni	2D	2.02	2.07	2.02	2.37	3.80	2.36
Ti ₂ Ni ₂	3D	2.27	2.05	2.05	2.05	2.05	2.46
TiNi ₃	3D	2.33	2.33	2.03	2.33	2.03	2.03
Al ₂ TiNi	2D	4.40	2.72	2.24	2.72	2.24	2.01
AlTi ₂ Ni	3D	2.73	2.73	2.27	2.37	2.04	2.04
AlTiNi ₂	2D	2.76	4.13	2.21	2.03	2.01	2.20

^a d_{ij} is the distance between atoms i and j . The geometries of the clusters and the labels of the atoms are as shown in Figure 1.

to find the global minimum-energy configuration of the system under consideration by starting with many randomly chosen different initial configurations than by starting with only a single initial configuration optimized through the methods mentioned above.⁵¹) For all these reasons, we have tried 1000 randomly generated initial configurations, within a volume of $7.5 \times 7.5 \times 7.5$ Å³, for each cluster under consideration. Each configuration then was relaxed, as an isolated cluster, through the MD simulations at low temperature, 1 K. The structure giving the minimum energy was then taken as the most stable structure for the cluster. The cluster geometries of the most stable structures obtained with the MD simulations are shown in Figure 1 (which correspond to the geometry of the cluster at the last MD step), and the corresponding interatomic distances are given in Table 2.

Starting with many randomly chosen different initial configurations assisted us in identifying the isomers of the clusters, so that we were able to determine the energy distribution of each species. Just as an example, for the Al₄ case, 1000 initial random geometries resulted in four distinct energy groups (so therefore four well-defined geometries), namely around 6.6 eV (equilateral pyramid), 6.5 eV (equilateral parallelogram), 5.9 eV (Y-shaped, like Al₂Ni₂ in Figure 1), and 5.3 eV (linear). We saw that each of the trial runs went into one of these four groups, not into any other energy (geometry). This situation

TABLE 3. Energy Distribution of the Clusters Studied^a

cluster	$-E(n)$						
Al ₄	6.6(12)	6.5(151)	5.9(567)	5.3(270)			
Ti ₄	7.9(52)	7.3(493)	6.7(455)				
Ni ₄	8.1(14)	7.8(326)	7.5(565)	7.3(27)	7.2(45)	6.7(23)	
Al ₃ Ti	6.5(46)	6.3(40)	6.2(221)	5.9(320)	5.6(200)	5.5(154)	5.4(19)
Al ₂ Ti ₂	8.7(409)	8.1(19)	7.6(230)	7.5(262)	5.7(76)	5.3(4)	
AlTi ₃	9.5(155)	9.0(842)	5.3(3)				
Al ₃ Ni	6.9(72)	6.7(59)	6.4(48)	6.1(288)	6.0(203)	5.6(100)	5.3(230)
Al ₂ Ni ₂	7.5(164)	7.4(81)	6.6(505)	6.5(21)	6.4(74)	6.3(30)	6.0(5)
	5.4(120)						
AlNi ₃	7.8(186)	7.5(345)	7.4(430)	5.7(34)	5.6(5)		
Ti ₃ Ni	9.0(54)	8.4(44)	7.9(340)	7.3(115)	7.1(130)	6.7(287)	
Ti ₂ Ni ₂	10.4(294)	9.5(267)	8.9(3)	8.5(283)	8.1(2)	6.9(8)	6.8(94)
	6.7(49)						
TiNi ₃	10.4(55)	10.3(853)	10.2(3)	9.5(2)	9.3(3)	9.1(18)	8.9(7)
	8.3(1)	7.2(58)					
Al ₂ TiNi	8.9(317)	8.4(23)	8.0(141)	7.7(130)	7.5(275)	6.4(1)	5.5(113)
AlTi ₂ Ni	10.1(180)	9.5(159)	9.1(658)	7.7(1)	5.4(2)		
AlTiNi ₂	9.8(604)	9.0(1)	8.8(20)	8.4(1)	7.9(365)	7.1(6)	6.7(3)

^a E is the total interaction energies of possible isomers via MD simulation. n represents the total number of trials giving the same energy.

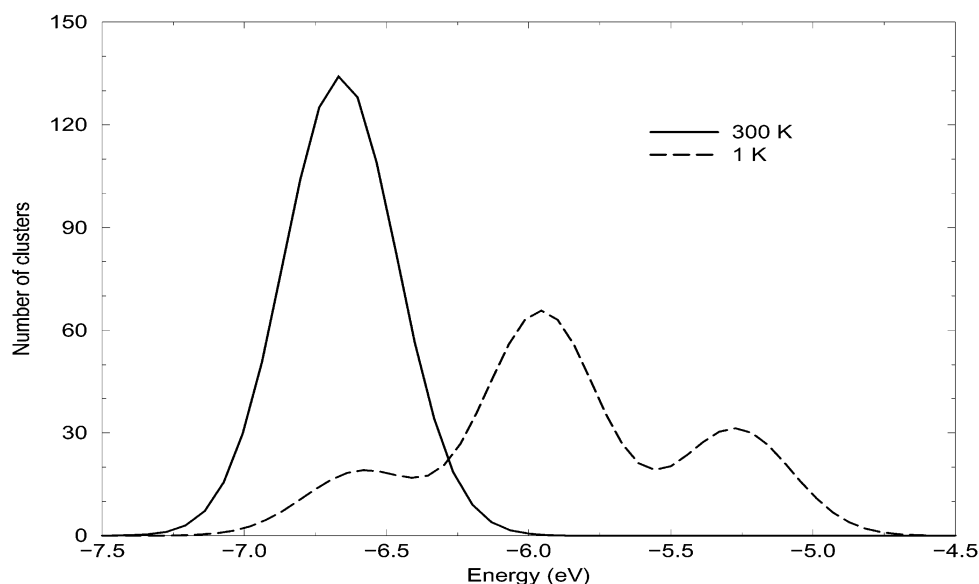


Figure 2. The Gaussian-broadened distributions (number of clusters possessing the energy between E and $E + dE$) of Al₄ clusters at 1 and 300 K.

was similar for all the remaining clusters. We tabulated the energy distribution data in Table 3. As seen from that table, the number of isomers varies from one species to another, according to their constituent atoms. As advertised previously, we saw indeed several “isomers” for each cluster, possessing geometries not similar at all to each other. That there exist only a few, finite number of local minima is the result of the fact that we chose our working temperature to be 1 K. At such a low temperature, it is natural for only low-energy states (geometries) to be populated. To see the effect of temperature on the energy levels (geometries) of the clusters, we performed another series of simulations at 300 K. We were again able to obtain the minimum energy geometries obtained at 1 K with some small distortions. Because the increased temperature adds some small amount of kinetic energy to the atoms, the minimum energies at 300 K were slightly larger (i.e. absolutely smaller) than those at 1 K (compare the third column with the last column in Table 4). The most striking difference between the studies at 1 and 300 K was that in the latter case there were no distinct energy groups (thus no well-defined geometries) at all. For all the clusters considered, we witnessed the same situation at 300 K. Put another way, the increased temperature caused high-

energy states (besides the low-energy states) to populate. To visualize this phenomenon clearly, we superimposed in Figure 2 the Gaussian-broadened distributions (for the number of clusters possessing the energy between E and $E + dE$) of Al₄ clusters at 1 and 300 K. It follows from this figure that the distinct energy groups at 1 K (corresponding to peaks in the dashed-line curve) disappear at 300 K (only one peak in the solid curve). Second, we see that the majority of randomly chosen different initial configurations result in structures with energy close to the global minimum. This means that 300 K for the Al₄ cluster (and for others also) should not be considered as *high temperature*.

Clusters differ from molecules which usually possess definite compositions and definite geometries. As mentioned above, the properties of a cluster depend on the number of constituent atoms as does the energetically most stable structure. Although a particular geometry may be more stable than any of several others, clusters generally can assume any of a number of different geometries. In low-temperature studies, like the present one, the number of distinct geometries is finite because the cluster does not have energy enough to pass over some “large” energy barriers on the potential energy surface. That is, the

TABLE 4. Calculated Interaction Energy by the DFT Method, $E_I(\text{DFT})$, and Total Potential Energy by Empirical Potential (through MD simulations at 1 K), $E_T(\text{MD})^a$

cluster	$-E_I(\text{DFT})$	$-E_T(\text{MD})$	$-E_2$	E_3	$100(E_3/E_2)$	$-E_T^{300\text{K}}(\text{MD})$
Al ₄	2.9054	6.6494	9.0208	2.3715	~26	6.6448
Ti ₄	9.4808	7.8733	9.7853	1.9120	~20	7.8674
Ni ₄	6.7985	8.0877	10.5045	2.4168	~23	8.0767
Al ₃ Ti	5.6978	6.5162	8.0612	1.5451	~19	6.5106
Al ₂ Ti ₂	5.2894	8.7285	8.8627	0.1343	~02	8.7240
AlTi ₃	8.7790	9.5257	10.9172	1.3915	~13	9.5209
Al ₃ Ni	5.6401	6.8813	8.2493	1.3680	~17	6.8720
Al ₂ Ni ₂	6.3613	7.4618	7.2686	-0.1933	~03	7.4335
AlNi ₃	7.8628	7.7821	8.2394	0.4573	~06	7.7576
Ti ₃ Ni	7.3243	9.0458	10.6066	1.5608	~15	9.0413
Ti ₂ Ni ₂	8.6911	10.3836	12.6011	2.2174	~18	10.3774
TiNi ₃	8.8924	10.3685	12.7273	2.3588	~19	10.3634
Al ₂ TiNi	7.0054	8.8912	9.1088	0.2169	~02	8.8882
AlTi ₂ Ni	8.5650	10.0629	11.3728	1.3099	~12	10.0601
AlTiNi ₂	8.2884	9.8224	10.0150	0.1926	~02	9.8199

^a Contributions of two- and three-body energies, E_2 and E_3 , to the total potential energy, $E_T(\text{MD})$, and their ratio are given separately. The last column gives the total energy at 300 K through MD simulations, $-E_T^{300\text{K}}(\text{MD})$. Energies are in eV.

atoms are trapped inside some finite number of “deep” local minima. As the temperature increases, the cluster will have energy enough to pass over from any local minimum to another, deep or not; consequently, a cluster may assume many stable structures at high temperatures different from those in low temperatures.

Information about most of the clusters considered in this work does not exist in the literature. We have encountered data of only Al₄ and Ni₄ tetramers. To our best knowledge, the present calculated values for the remaining 13 clusters are the first to appear. In the following, we will compare the present results for Al₄ and Ni₄ with those from the literature. We will focus mainly on the structures of the four-atom clusters considered, not on the bond lengths. The geometry concern is not only the most intriguing question in the short history of the clusters, but also one of the most difficult aspects to probe. Because of the approximations made, the theoretical calculations usually result in the equilibrium geometries that are not accepted unanimously. Even in a simple case of homonuclear tetramers, we have seen that there was no consensus about the question of whether the considered species was 2D or 3D.

Al₄: In this study, we found the most stable geometry of Al₄ to be a 3D tetrahedron with T_d symmetry (see Figure 1). Pacchioni and Koutecký⁵² considered pseudopotential calculations and found that rhombic Al₄ was energetically most favorable. With an ab initio pseudopotential method, Upton⁵³ found that Al did not become 3D for Al₄, and the planar structures remained most stable. In his later perturbed electron drop model calculation, Upton⁵⁴ reported that the Al₄ cluster having lowest energy is in a puckered rhombohedron structure that is between the square-planar and tetrahedral geometries. Pettersson et al.⁵⁵ considered both ab initio and parametric empirical potential calculations for Al_n clusters, and they found the planar rhombus structure for Al₄ to be the lowest in energy. In the study of Erkoç⁵⁶ with a PEF, the tetrahedral form of Al₄ was reported to be most stable. In their empirical PEF calculation, Erkoç and Katiroğlu⁵⁷ calculated that the planar rhombus and the 3D tetrahedron structures were energetically very close to each other, but the tetrahedron geometry with T_d symmetry was slightly lower in energy. Jones,⁵⁸ using DFT calculation, found that the planar rhombohedral structure (D_{2h}) was more stable. Employing the MD technique, El-Bayyari and Erkoç⁵⁹ found a distorted tetrahedron as being most stable. Finally, with a first-principles calculation and a local orbital DFT study, Yang et al.⁶⁰ found a (nearly) rhombus as being

most stable for Al₄. In passing, for detailed information about Al clusters see ref 61.

Ni₄: Experimental observation of Parks et al.⁶² showed that the structure of Ni₄ was not certain; it was probably two-dimensional such as rhombic. In this study, we also found the most stable geometry of Ni₄ to be a 2D rhombus (see Figure 1). In his extended Hückel and complete neglect of differential overlap (CNDO) calculations, Baetzold⁶³ reported a pyramidal structure for Ni₄ as most stable. In the literature, there are many studies showing the tetrahedron geometry with T_d symmetry for Ni₄ energetically most favorable: Empirical PEF calculations of Erkoç,^{56,64} Amerillas and Garzon,⁶⁵ and Nayak et al.;⁶⁶ effective medium calculations of Stave and DePristo⁶⁷ and Wetzel and DePristo;⁶⁸ tight-binding MD calculations of Lathiotakis et al.⁶⁹ and Bouarab et al.;⁷⁰ and size-dependent empirical PEF calculation of Erkoç et al.⁷¹ A DFT calculation of Reuse and Khanna⁷² gave the stable structure of Ni₄ as trigonal bipyramid and square. Finally, in their empirical PEF calculation, Hu et al.⁷³ found Ni₄ as a trigonal pyramid.

DFT Calculation Results. With the aim of predicting the electronic properties of the most stable clusters obtained from MD simulations, we have performed DFT calculations within the effective core potential (ECP) level [with B3LYP exchange-correlation contribution]. In Table 4 we present the interaction energy, $E_I(\text{DFT})$, calculated by the DFT method with the total potential energy, $E_T(\text{MD})$, calculated by the empirical potential (through MD simulations). The interaction energy $E_I(\text{DFT})$ of the four-atom clusters was calculated by using

$$E_I = E_{\text{total}}^{\text{ABCD}} - E_{\text{total}}^{\text{A}} - E_{\text{total}}^{\text{B}} - E_{\text{total}}^{\text{C}} - E_{\text{total}}^{\text{D}} \quad (4)$$

where E_{total} are the total energies obtained from the DFT calculations for four-atom clusters (ABCD) and individual atoms (A, B, C, D). We see from Table 4 that there are some small discrepancies between the two types of calculations, as one should expect. However, the discrepancy for Al₄ is quite large, which is an exceptional case. The existence of small discrepancies in the potential energies of the two methods should not be surprising. One should not expect the two energy values to have the same value: during the parametrization process of PEF, there were many quantities (bond length, interaction energies, and geometries of dimers and trimers) re-obtained altogether as close as those resulting from experiments and, at the same time, those resulting from the previous ab initio results. This many-quantity process indispensably creates some amount of discrepancy between the two types of energy values.

TABLE 5. Possible Dissociation Channels and the Corresponding Dissociation Energies (in eV) for the Clusters Studied

cluster	dissociation channel	dissociation energy	cluster	dissociation channel	dissociation energy	cluster	dissociation channel	dissociation energy
Al ₄	→ Al ₃ + Al	−0.2194	Al ₃ Ti	→ Al ₂ Ti + Al	−1.8891	Al ₂ TiNi	→ AlTiNi + Al	−1.5697
	2Al ₂	−1.9993		Al ₃ + Ti	−3.0119		AlTi + AlNi	−1.5835
	Al ₂ + 2Al	−2.4525		Al ₂ + AlTi	−3.1739		Al ₂ Ni + Ti	−1.7523
	4Al	−2.9054		AlTi + 2Al	−3.6270		Al ₂ Ti + Ni	−3.1967
Ti ₄	→ Ti ₃ + Ti	−3.6408	Al ₃ Ni	→ Al ₂ Ni + Al	−0.3870	AlTi ₂ Ni	→ Ti ₂ Ni + Al	−1.6075
	2Ti ₂	−3.6849		Al ₂ + AlNi	−1.8359		AlNi + Ti ₂	−2.3159
	Ti ₂ + 2Ti	−6.5829		AlNi + 2Al	−2.2890		AlTi ₂ + Ni	−2.6109
	4Ti	−9.4808		Al ₃ + Ni	−2.9541		AlTiNi + Ti	−3.1293
Ni ₄	→ Ni ₃ + Ni	−0.8549	Ti ₃ Ni	→ Ti ₂ Ni + Ti	−0.3668	AlTiNi ₂	→ TiNi ₂ + Al	−1.3085
	2Ni ₂	−4.2822		Ti ₃ + Ni	−1.4843		AlNi + TiNi	−2.1341
	Ni ₂ + 2Ni	−5.5404		Ti ₂ + TiNi	−1.6231		AlTiNi + Ni	−2.8527
	4Ni	−6.7985		Ti ₂ + Ti + Ni	−4.4263		AlNi ₂ + Ti	−3.4004
Al ₂ Ti ₂	→ AlTi ₂ + Al	+0.6646	AlTi ₃	→ AlTi ₂ + Ti	−2.8250	AlTiNi ₂	AlNi + Ti + Ni	−4.9373
	2AlTi	−1.1478		Ti ₃ + Al	−2.9390		AlTi + Ni ₂	−4.9595
	Al ₂ Ti + Ti	−1.4807		Ti ₂ + AlTi	−3.8103		TiNi + Al + Ni	−5.4852
	Al ₂ + Ti ₂	−1.9384		Ti ₂ + Al + Ti	−5.8811		AlTi + 2Ni	−6.2176
	2Al + Ti ₂	−2.3915	AlNi ₃	→ Ni ₃ + Al	−1.9192		Ni ₂ + Al + Ti	−7.0303
	AlTi + Al + Ti	−3.2186		AlNi ₂ + Ni	−2.9748		Al + Ti + 2Ni	−8.2884
	Al ₂ + 2Ti	−4.8363		Ni ₂ + AlNi	−3.2536			
	2Al + 2Ti	−5.2894		AlNi + 2Ni	−4.5117			
Al ₂ Ni ₂	→ 2AlNi	+0.3409	TiNi ₃	→ TiNi ₂ + Ni	−1.9125			
	Al ₂ Ni + Ni	−1.1082		Ni ₃ + Ti	−2.9488			
	AlNi ₂ + Al	−1.4733		Ni ₂ + TiNi	−4.8310			
	AlNi + Al + Ni	−3.0102		TiNi + 2Ni	−6.0891			
	Al ₂ + Ni ₂	−4.6501		Ni ₂ + Ti + Ni	−7.6342			
	2Al + Ni ₂	−5.1032		3Ni + Al	−7.8628			
	Al ₂ + 2Ni	−5.9082						
	2Al + 2Ni	−6.3613						
Ti ₂ Ni ₂	→ TiNi ₂ + Ti	−1.7112						
	Ti ₂ Ni + Ni	−1.7337						
	2TiNi	−3.0846						
	Ti ₂ + Ni ₂	−4.5350						
	Ti ₂ + 2Ni	−5.7932						
	TiNi + Ti + Ni	−5.8879						
	2Ti + Ni ₂	−7.4330						
	2Ti + 2Ni	−8.6911						

TABLE 6. Some Molecular Properties of the Clusters Studied^a

cluster	N _b	N _g	N _α	N _β	cluster	N _b	N _g	N _α	N _β
Al ₄	48	64	6	6	AlNi ₃	114	220	29	28
Ti ₄	136	272	24	24	TiNi ₃	136	272	33	33
Ni ₄	136	272	36	36	Ni ₂ Ti ₂	136	272	30	30
Al ₃ Ti	70	116	11	10	Ti ₃ Ni	136	272	27	27
Al ₂ Ti ₂	92	168	15	15	Al ₂ TiNi	92	168	18	18
AlTi ₃	114	220	20	19	AlTi ₂ Ni	114	220	23	22
Al ₃ Ni	70	116	14	13	AlTiNi ₂	114	220	26	25
Al ₂ Ni ₂	92	168	21	21					

^a N_b is the number of basis functions with symmetry A; N_g is the number of primitive Gaussians; N_α is the number of α-electrons; N_β is the number of β-electrons. The point group symmetry of all the clusters is C₁.

In Table 4 we also give the contributions of the two- and three-body energies, E_2 and E_3 , to the total energy, $E_T(\text{MD})$, and the percentage ratio of E_3 to E_2 . It is seen that, for all clusters but Al₂Ni₂, the three-body interaction is positive. That the mentioned percentage ratio varies between 2% to 26% indicates that the contribution of the three-body energies to the total energy is not at all negligible. This point is one of the most important conclusions to be drawn from this work. As an aside, a comparison of the geometries in Figure 1 with the E_3 values in Table 4 shows no correlation.

We calculated the possible dissociation channels and the corresponding dissociation energies, which are tabulated in Table

TABLE 7. HOMO and LUMO Energies (in Hartrees) and the HOMO-LUMO Gap (E_g) Energies (in eV) of the Clusters Studied, Calculated by the DFT Method

cluster	HOMO(α)	LUMO(α)	$E_g(\alpha)$	HOMO(β)	LUMO(β)	$E_g(\beta)$
Al ₄	−0.1511	−0.1281	0.6239			
Ti ₄	−0.1477	−0.0878	1.6324			
Ni ₄	−0.1614	−0.1175	1.1940			
Al ₃ Ti	−0.1715	−0.1128	1.5959	−0.1640	−0.1156	1.3184
Al ₂ Ti ₂	−0.1474	−0.1392	0.2253			
AlTi ₃	−0.1549	−0.0973	1.5695	−0.1558	−0.0906	1.7741
Al ₃ Ni	−0.1450	−0.1200	0.6803	−0.1520	−0.1308	0.5761
Al ₂ Ni ₂	−0.1665	−0.1189	1.2955			
AlNi ₃	−0.1653	−0.1027	1.7034	−0.1509	−0.1042	1.2716
Ti ₃ Ni	−0.1448	−0.0903	1.4838			
Ti ₂ Ni ₂	−0.1488	−0.1033	1.2400			
TiNi ₃	−0.1304	−0.1016	0.7839			
Al ₂ TiNi	−0.1537	−0.1033	1.3722			
AlTi ₂ Ni	−0.1663	−0.0992	1.8253	−0.1580	−0.0969	1.6629
AlTiNi ₂	−0.1582	−0.1039	1.4789	−0.1557	−0.1022	1.4552

5. We define the dissociation energy of a dissociation process $XY \rightarrow X + Y$ as $E_{\text{dis}} = E_{\text{total}}^{\text{XY}} - E_{\text{total}}^{\text{X}} - E_{\text{total}}^{\text{Y}}$. In calculating the dissociation energies, we used the total energy values obtained from the DFT calculations: the four-atom cluster values are given in Table 4, the three-atom, two-atom, and atomic energies were from our previous work.²⁵ We see from Table 5 that, apart from Al₂Ti₂ and Al₂Ni₂, all the dissociation energies are

TABLE 8. Excess Charge (in units of electron charge) on Atoms and Dipole Moments (in Debye) of the Clusters Studied, Calculated by the DFT Method^a

cluster	q_1	q_2	q_3	q_4	μ_x	μ_y	μ_z	μ
Al ₄	-0.0268	0.0269	-0.0269	0.0268	0.8673	1.6234	0.8844	2.0420
Ti ₄	0.0790	-0.0872	-0.0835	0.0917	0.0697	0.1563	-0.0422	0.1763
Ni ₄	0.0616	0.0559	0.0205	-0.1379	-1.6355	-0.2655	0.0056	1.6569
Al ₃ Ti	0.1562	0.1283	0.0180	-0.3025	-3.6227	0.1875	0.1318	3.6299
Al ₂ Ti ₂	0.3669	0.3563	-0.3338	-0.3894	0.3485	-0.0814	0.0105	0.3580
AlTi ₃	0.4504	-0.0939	-0.1537	-0.2029	-0.0952	0.4175	-2.9069	2.9382
Al ₃ Ni	0.2793	0.2802	0.2773	-0.8367	-0.1216	0.9202	-0.0947	0.9330
Al ₂ Ni ₂	0.2811	0.2804	-0.5796	0.0181	-0.3577	-0.0017	-0.0033	0.3577
AlNi ₃	0.3997	-0.3926	-0.0130	0.0060	0.8578	0.3558	0.0388	0.9295
Ti ₃ Ni	1.2408	-0.3679	-0.4749	-0.3980	0.0613	2.2782	0.0024	2.2790
Ti ₂ Ni ₂	0.3729	0.3716	-0.3711	-0.3735	-0.0059	0.0113	1.7503	1.7504
TiNi ₃	0.0565	0.0413	0.0810	-0.1789	0.4601	0.0583	2.5934	2.6345
Al ₂ TiNi	0.3390	0.3391	-0.3606	-0.3175	-0.0001	3.5117	0.0000	3.5117
AlTi ₂ Ni	0.2586	-0.3650	-0.3622	0.4686	-2.5010	0.0208	-0.3777	2.5295
AlTiNi ₂	0.3409	-0.2609	0.1462	-0.2263	-0.5620	0.8948	0.0086	1.0567

^a Refer to Figure 1 for the labels of atoms.

negative, as should be. The positive ones should not be interpreted as a simultaneous dissociation or as unstable clusters. This is due to the fact that although the dimers and trimers of our previous work²⁵ were calculated thoroughly by using the DFT method, the tetramers of the present work were calculated by using first the MD method and then the DFT method. Consequently, the optimized structures of Al₂Ti₂ and Al₂Ni₂ obtained from MD simulations might not correspond, at least in energy, to the minimum-energy configuration that would be obtained by using only the DFT method. Nevertheless, Table 5 is illustrative and is believed to give reasonable trends for dissociation channels. It is seen for each cluster that atomization energies (dissociation to the constituent atoms) are, not surprisingly, the greatest among the other possible dissociation energies. Homonuclear tetramers X₄ are seen to dissociate as X₄ → X₃ + X, as expected. Apart from Al₂Ni₂ and AlTi₃, the remaining Al-contained clusters prefer to fragment to give one Al atom first. Al₂Ni₂ dissociates to give two AlNi dimers, consistent with the fact that the AlNi dimer has a large binding energy (3.3511 eV, ref 25). Except for AlNi₃, all XY₃-type clusters dissociate as XY₂ + Y. For the NiTi-containing species, we see that there is no priority for either Ni or Ti to dissociate first. If you combine this data with the fact that Al has a relatively larger preference to dissociate first, we may conjecture the following: If we continue to enlarge our AlTiNi ternary system, we expect most of the Al atoms to occupy the outermost part of the system, and relatively few to displace themselves in the NiTi-rich inner part.

Some computational details in the DFT calculations are presented in Table 6, which contains mainly the molecular properties, the basis set, and spin information of the species considered. Basis information reflects the basis set used in the calculation, namely CEP-121G. The size of the basis set is fixed for each element in CEP-121G. The accuracy of results depends surely on the basis set used. In the present study the basis set used is believed to be sufficient for the species under study.^{48–50}

The positions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the HOMO-LUMO difference (or the frontier molecular orbital energy gap, E_g) bear some importance from the spectroscopic point of view. Since the number of electrons in Al₄, Ti₄, Ni₄, Ni₃Ti, Ni₂Ti₂, NiTi₃, and Al₂TiNi is even, these clusters have only α -states; on the other hand, the remaining clusters have an odd number of electrons hence they have both α - and β -states. The HOMO, LUMO, and E_g values of the

systems studied are tabulated in Table 7. Some interesting features follow from this table: its $E_g(\alpha)$ value tempts us to say that the Al₂Ti₂ cluster has the best metallic property, but we should remember that a four-atom cluster is too small to be classified as conducting or not. Another feature is that the gap of α states is relatively larger than that of β states, except for AlTi₃. An interesting situation draws attention: a replacement of one Al atom by a Ni atom increases the $E_g(\alpha)$ value of Al₂Ti₂ by about eight times. This may be due to the drastic change in the geometry in passing from Al₂Ti₂ to AlTi₂Ni. The same situation takes place also in passing from Al₂Ti₂ to Al₃Ti and/or AlTi₃.

The calculated excess charge (Mulliken charges) and dipole moments of the four-atom clusters are given in Table 8. We note that all the clusters bear a net dipole moment according to their geometry and configurations of constituent atoms, as expected. Because of its rotational symmetry, the homonuclear Al₄ tetramer with a tetrahedral structure experiences relatively less charge accumulations on the atoms, compared to the other clusters. But its resulting dipole moment is, however, not small because of the distribution of the excess charges among the atoms. The same distribution concern makes the Ti₄ cluster possess the smallest dipole moment. One of the important outcomes of the charge data from this table is that in all heteronuclear clusters containing Al (i.e., Al₃Ti, Al₂Ti₂, AlTi₃, Al₃Ni, Al₂Ni₂, AlNi₃, Al₂TiNi, AlTi₂Ni, and AlTiNi₂) we never see a negative charge accumulation on Al atoms. A very similar conclusion holds for Ni atoms in species Ni₃Ti, Ni₂Ti₂, and NiTi₃. Another interesting feature is the unexpected situation between the symmetry of the structure and the charge distribution in clusters Ti₄ and Ni₄. We see that although the charge accumulation in Al₄ is commensurate with its geometry, the similar expected situation does not occur in Ti₄ and Ni₄: charges on the atoms of each of these clusters do not show any correlation in their geometry at all.

In this study, we focused on the structural and electronic properties of Al_kTi_lNi_m ($k + l + m = 4$) clusters by carrying out MD simulations and DFT calculations. We placed the main emphasis on MD results. We first parametrized a PEF for the AlTiNi ternary system, which includes the two- and three-body interactions. We saw that the contribution of the three-body energy to the total energy is not negligible. We then determined the most stable structures of the clusters considered by MD simulations. We witnessed several “isomers” for each species studied, having geometries not similar to each other. We chose

the cluster that has the lowest energy as the most stable structure. The number of isomers at 1 K was few, whereas at 300 K it was denumerably many. All of the following were expected: the increasing temperature causes the high-energy states, as well as the low-energy states, to populate. We then calculated the possible dissociation channels and electronic properties of the most stable structures by the DFT method. From the dissociation data, we conjectured that if the AlTiNi system is gradually enlarged, most of the Al atoms are expected to displace themselves in the outermost part of the system, relatively few occupying the NiTi-rich inner part. On the occasion of this work, we propose to continue our research series toward the larger clusters of the AlTiNi system, hoping that they give rise to valuable insights into the evolution from small clusters to the bulk AlTiNi system. In addition, studies on larger clusters of this material might shed light on how the *shape memory* mechanism works at the atomic level.

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