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Structural and electronic properties of $\mathrm{Al}_k\mathrm{Ti}_l\mathrm{Ni}_m$ microclusters: Density-functional-theory calculations

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Structural and electronic properties of $\mathrm{Al}_k\mathrm{Ti}_l\mathrm{Ni}_m(k+l+m=2,3)$ microclusters have been investigated by performing density-functional-theory calculations within the effective core potential level. Dimers and trimers of the elements aluminum, titanium, and nickel, and their binary and ternary combinations have been studied in their ground states. The optimum geometries, possible dissociation channels, vibrational properties, and electronic structure of the clusters under study are obtained.

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I. INTRODUCTION

Quantum molecular methods in cluster theory have proven its usefulness in quantum chemical investigations of the structural and electronic properties of small atomic and molecular clusters. The theoretical and experimental results of these studies, their far-reaching consequences, and their practical and possible industrial applications have been collected in several reviews [1–7] and books [8–22]. At the fundamental level, these investigations are being carried out in order to reveal the very general physical and chemical properties of atoms under the specific conditions existing in clusters and therefore to reach a consensus in interpreting the basic properties of clusters.

Clusters are on the border that separates molecules from liquids and solids [16,17]. From atoms and molecules to liquids and solids, the evolution of structural and electronic properties of solid state is understood with the help of the studies of small clusters. Among these studies are abundances [6,23], catalysis [14,20,24–36], chemisorption and substrate adsorption [28–31,35,37–50], crystal growth [2,51–56], electronic structures, equilibrium structures, evolution of surface properties [57,58], laser applications [31], magic numbers [2,5,14,59–74], magnetism [47,66,69,70,75–84], nucleation [26,27,31,50,55,57,85–88], photographic processes [27,31,36], reactivity [14,36,89–91], and properties as a function of clusters size [3,30,41,58,59,70,75,76,90,92–101]. All the other informations about the studies not mentioned above can be drawn from Refs. [1–22]. In addition to the theoretical studies (see Ref. [102] for a somewhat detailed description of the methods), experiments constitute the very indispensable part of the field of cluster research. This ceaseless interplay between theory and experiment leads to new scopes in understanding of the properties of clusters.

The structural and electronic properties of trimers and higher clusters have been less well investigated compared to those of dimers in the literature of clusters. Structural properties of these bear particular importance because one can begin only with the trimer to compare between cluster properties and those of the bulk [103]. For example, the structure of small clusters of group-IA and group-IB metals have been predicted to be linear. Therefore one can expect some ‘‘critical’’ cluster sizes to exist, at which some drastic structural changes take place leading to the close packing of the bulk [6,69,80,82,103,104]. Geometrical arrangement of the atoms and the charges on them in small clusters constitute another aspect of the importance in understanding of same catalytic processes [26]. Therefore, determining geometrical and electronical properties of small clusters is worthwhile.

There are lots of experimental and theoretical studies which showed that the geometrical and electronic properties of small clusters exhibit no similarity at all compared with the properties corresponding to the bulk. This is perhaps the reason that has rendered the cluster area to be one of the most actively studied research field. There is another intriguing phenomenon, the so-called ‘‘magic numbers’’ that has given intense impetus to many researchers. Simply, at magic numbers, clusters are unusually stable. In the mass-spectroscopic detection of clusters, it is usually the case where especially high abundances for certain cluster sizes are found. The existence of magic numbers is still waiting for a concrete explanation.

In the literature, the transition-metal (TM) clusters have a special place because of their physical, chemical, and obvious economical importance. For this reason, TM clusters have drawn very intense interest. Three monumental reviews, Refs. [1–3], present the experimental data and theoretical results concerning TM clusters. Another well-known review [5] giving both theoretical and experimental information about the heavy *p*-block dimers and trimers is very precious. Because of their widespread use in the studies of the catalysis processes, chemisorption and substrate adsorption, nucleation, the photographic processes, and possible laser applications, the chemistry of transition metals, especially of bare metal clusters and of metallic surfaces has a great importance [20,26,32,85]. In addition, the diatomic transition metals are source of information about the metal-metal bond and organometallic complexes [105]. These dimers have an important place in solid-state physics; they play a key role in exploring how the atomic properties change as the atoms are clustered [32]. Homonuclear TM diatomics are the simplest models for metallic clusters and binuclear TM complexes.

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They also have theoretical, astronomical, and high temperature importance [106,107]. Therefore, studying their properties would be very useful and instructive.

The microclusters of aluminum, nickel, titanium, and their mixtures have been considered in this paper. From the metallurgical point of view, their binary and ternary alloy systems have become very popular. Their crystal structure, phase diagram data, electronic structure, optical properties, etc. have been investigated intensely. There exist some experimental and theoretical studies about Al-Ti-Ni binary and ternary alloy systems [108–110], the Ni-Ti alloy system [111,112], the Al-Ti alloy system [113,114], and the Al-Ni alloy system [115,116]. This intense interest in these elements is due partly to their shape-memory-alloy properties that render them industrially important.

In the present study, structural and electronic properties of sixteen different microclusters of the type $\mathrm{Al}_k\mathrm{Ti}_l\mathrm{Ni}_m(k+l+m=2,3)$ have been investigated. The dimers (Al_2, Ti_2, Ni_2), trimers (Al_3, Ti_3, Ni_3) of elements aluminum, titanium, and nickel, and their binary combinations (AlNi, AlTi, NiTi, Al_2Ni, $AlNi_2$, Al_2Ti, Ni_2Ti, $AlTi_2$, $NiTi_2$), and ternary combination (AlTiNi) have been studied in their ground states. The density-functional-theory (DFT) calculations have been performed within the effective core potential (ECP) level [with B3LYP exchange-correlation contribution]. All the calculations have been carried out by using the GAUSSIAN 98 package [117]. The calculated spectroscopic constants (binding energy D_e, equilibrium interatomic separation r_e, and fundamental frequency w_e) of the dimers and the minimum energy configurations of the trimers (bond lengths and bond angles, as well as their fundamental frequencies w_n) are reported. For all the microclusters 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 trimers are also given. The calculated values are compared with the previously reported ones computed by various other approximate methods and estimated experimentally. Several discrepancies appear between the present calculations and some literature values.

II. METHOD OF CALCULATION

Why *density-functional theory* and *effective core potential* methods? When the standard quantum-mechanical methods are too time consuming or incapable, the density-functional theory provides us with the formal framework for energy calculations with predictive value. Even when working with the density-functional theory, one usually encounters some great computational difficulties in treating systems with atoms having many electrons. The *effective core potential* or *pseudopotential* methods have been indispensable in partially overcoming these difficulties. In these methods, instead of considering all the electrons (all-electron *ab initio* methods), one treats only the valence electrons explicitly; the remaining ‘‘effective core’’ electrons are thought to modify the potential in which the valence electrons move. (For a review, see Ref. [2], and references therein.) The effective core potential methods have proven their accuracy and reliability over many years; they give good results for chemical systems, with error relative to the experiment comparable to corresponding error obtained from all-electron *ab initio* methods [30].

In the present study, $\mathrm{Al}_k\mathrm{Ti}_l\mathrm{Ni}_m(k+l+m=2,3)$ microclusters have been investigated theoretically by performing density-functional-theory calculations [118]. The exchange and correlation potential contributions have been considered at B3LYP level [119]. The compact effective potential (CEP) basis functions with ECP triple-split basis, namely, CEP-121G [120–122], have been used in the calculations. The exchange term of B3LYP consists of hybrid Hartree-Fock (HF) and local spin density (LSD) exchange functions with Becke’s gradient correlation to LSD exchange [123]. The correlation term of B3LYP consists of the Vosko, Wilk, and Nusair (VWN3) local correlation functional [124] and Lee, Yang, and Parr (LYP) correlation correction functional [125]. The BLYP method gives a better improvement over the SCF-HF results. Its predictions are in qualitative agreement with the experiment. In general, the DFT method overestimates the energies, and it gives shorter bond lengths than the experimental values. However, the optimized structures predicted at BLYP level are in good agreement with the experiment [126,127].

CEP-121G basis functions are becoming widely used in quantum chemistry, particularly in the study of compounds containing heavy elements [120–122]. The CEP basis sets have been used to calculate the equilibrium structures and spectroscopic properties of several small molecules [120]. The standard basis set of CEP theory was consistent for the entire series not only within the lanthanide series but also with the second- and third-row metals. The quality of the CEP-121G basis set does not degrade when going from the second to the third row of the periodic table. In the present calculations, CEP-121G basis set and the number of primitive Gausssians used in CEP-121G vary from atom to atom, depending on the valence structure of atoms considered. In the present paper, the optimized ground-state structures, electronic properties, and vibrational spectra of $\mathrm{Al}_k\mathrm{Ti}_l\mathrm{Ni}_m(k+l+m=2,3)$ microclusters for sixteen different species have been calculated.

III. RESULTS AND DISCUSSIONS

A. Dimers

The calculated results, as well as some experimental and theoretical outcomes from the literature, related to homonuclear dimers Al_2, Ni_2, and Ti_2 are presented in Tables I–III.

Al_2. The Al-Al bond in the bulk metal is 2.86 Å [128], as compared with our value of 2.65 Å. The corresponding experimental value, estimated from vibrational spectra of aluminum, is 2.70 Å [129], which is very close to the present calculation. As is seen from Table I, both experimental and theoretical values for Al-Al bond are all in a good range of 2.45–2.95 Å, most of them are close to the experimental value of 2.70 Å. This is not surprising because aluminum is

TABLE I. Spectroscopic constants of Al_2. Binding energy D_e is in eV, equilibrium interatomic separation r_e is in Å, and the fundamental frequency ω_e is in cm^{-1}.

D_e	r_e	ω_e	Method	Reference
0.4531	2.6520	274.3	DF	This work
1.5	2.466	350.0	Expt.	[132]
1.55			Expt.	[133]
	2.70	284.2	Expt.	[129]
1.33	2.51	354	*ab initio* (pseudopotential)	[41]
	2.95	246	DF	[59]
1.425	2.73	277	SOCI+Q BIG-ANO	[94]
	2.51		First-principles calculations	[95]
1.51	2.519		*ab initio* and par. emp. potential	[96]
2.03	2.70	290	DF	[97]
1.19	2.779	270	MCSCF+FOCI	[134]
2.0			LDA	[130]
0.08	2.65		DF	[135]
1.35	2.717	285	CCD+ST	[136]
1.30	2.493	338	MRCI+D	[137]

TABLE II. Spectroscopic constants of Ni_2. Binding energy D_e is in eV, equilibrium interatomic separation r_e is in Å, and the fundamental frequency ω_e is in cm^{-1}.

D_e	r_e	ω_e	Method	Reference
1.2581	2.4948	222.2	DF	This work
		330	Expt.	[27]
2.068	2.200		Expt.	[32]
2.08			Expt.	[99]
		192	Expt.	[106]
2.3			Expt.	[132]
2.38			Expt.	[133]
2.03			Expt. and abs. ent. method	[138]
2.36	2.30	325	Expt. and second-law calculations	[138]
		381	Expt.	[139]
		280	Expt.	[140]
2.62	2.5		EH	[24]
	2.5		MO	[26]
1.42	2.20	289	CI	[28]
0.97	2.60	236	HF	[28]
1.89	2.26	(190)	ECP-GVB-CI	[29]
1.43	2.33	211	ECP-CI	[30]
1.21	2.36	201	ECP−one-pair CI	[30]
0.92	2.33	216	ECP-SCF	[30]
	2.28	240	RHF	[31]
	2.49		ECP-MCSCF	[38]
3.32	2.00		DF	[76]
2.4			CNDO	[92]
2.92	2.04	344	ECP-GVB-CI	[105]
2.78	2.21	395	MEH	[107]
2.45	2.21	370	EH	[141]
2.70	2.18	320	DF	[142]

TABLE III. Spectroscopic constants of Ti_2. Binding energy D_e is in eV, equilibrium interatomic separation r_e is in Å, and the fundamental frequency ω_e is in cm^{-1}.

D_e	r_e	ω_e	Method	Reference
2.8979	1.8537	482.4	DF	This work
		407.9	Expt.	[85]
1.3			Expt.	[132]
1.31			Expt.	[133]
1.23			Expt. and second-law calculations	[143]
1.42	2.65	288	Expt. and third-law calculations	[143]
	3.0		MO	[26]
	1.87	580	RHF	[31]
1.88	2.30	250	EH	[141]
2.30	2.52	220	DF	[142]
	1.96		DV-$X\alpha$	[144]

almost an ideal free-electron metal. It is light and has only one isotope. These properties render it to be one of the model systems for testing and developing ideas about metal clusters. It is possible to perform reasonably reliable theoretical calculations on aluminum clusters [131]. The calculated binding energy D_e for Al_2 of 0.45 eV is significantly lower than the experimental estimate of ~1.5 eV [132,133]. This is in contrast with the general trend of the DFT method because, as it was mentioned before, the DFT method, in general, overestimates the energies with respect to the experimental values. The fundamental frequency ω_e is calculated to be 274.3 cm^{-1}, in reasonable agreement with the experimental value of 284.2 cm^{-1} [129]. For more rigorous treatments for Al_2 involving low-lying states, the reader is recommended to refer to Refs. [94,134–137].

Ni_2. The ground state is found to have a bond length of 2.4948 Å, which is surprisingly (and incidentally) close to the bulk value of 2.4919 Å [128]. The discrepancy between the present result and the seemingly best estimate of 2.200 Å of the experiment [32], which was on jet-cooled Ni_2, is not too severe. On the other hand, the case for the binding energy cannot, however, be seen as a reliable one: the ground state is found to have a binding energy of 1.2581 eV that is not at all close to the corresponding experimental value of 2.068 eV. Similar to Al_2, the present binding energy is much lower than the experimental one, again not consistent with the general trend of the DFT method. As is seen from Table II, the other calculated D_e values vary in a large range from 1.42 to 3.42 eV, i.e, there is no unanimous answer concerning the binding energy of Ni_2 in the literature. The situation for the fundamental frequency ω_e is even more severe: both experimental estimates and other theoretical calculations exhibit a great diversity; the present value of 222.2 cm^{-1} lies between the two extrema of 192 and 395 cm^{-1}.

Ti_2. The Ti-Ti bond is calculated to be 1.8537 Å, lower than the bulk value of 2.95 Å [128] and the conjectured value of 2.65 Å used by Kant and Lin [143] in his semiempirical calculations. We have not encountered any other experimental value for the bond length to compare. The other calculated results for r_e taken from the literature again do not show any unanimity. The binding energy D_e of Ti_2 is calculated as 2.8979 eV, which is significantly overestimated compared with the experimental estimate of ~1.3 eV [132,133,143] and with the other theoretical calculations. In this case, the results for both bond length and binding energy is consistent with the typical outcomes of the DFT method. The fundamental frequency ω_e is calculated to be 482.4 cm^{-1}, which may be considered to be much closer to the experimental prediction of 407.9 cm^{-1} [85] (matrix-isolated Ti_2) than the other calculated values, cited in Table III.

AlNi, *AlTi*, *NiTi*. For these heteronuclear diatoms, there were no experimental and theoretical data to compare in the literature. However, relatively more information is available about many of the homonuclear metal dimers. To the best of our knowledge, the present calculated values are the first for these species. Calculated spectroscopic constants for these dimers are given in Table IV.

B. Trimers

The present calculated results for the homonuclear trimers Al_3, Ni_3, and Ti_3, with some experimental and theoretical values from the literature, are tabulated in Table V. In the following discussion, we will focus mainly on the structure of the trimers considered. This 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 the simplest case of homonuclear trimers,

TABLE IV. Spectroscopic constants of heteronuclear diatoms. Binding energy D_e is in eV, equilibrium interatomic separation r_e is in Å, and the fundamental frequency ω_e is in cm^{-1}.

Diatom	D_e	r_e	ω_e	Method	Reference
Al-Ni	3.3511	2.5331	263.5	DF	This work
Al-Ti	2.0708	2.7480	202.9	DF	This work
Ni-Ti	2.8032	2.0567	349.3	DF	This work

TABLE V. Trimers Al_3, Ni_3, and Ti_3 at minimum energy configurations. Bond lengths $a=b$ are in Å, bond angle θ is in deg, and the vibration with maximum amplitude ω^* is in cm^{-1}. The geometry, with $a=b$, is as shown in Fig. 1.

Trimer	Structure	a	θ	ω^*	Method	Reference
Al_3	Equilateral	2.64		200.7	DF	This work
	Equilateral (D_{3h})	2.802			Expt. and MO	[148]
	Triangular (C_{2v})	2.709	72.6		Expt. and MO	[148]
	Triangular	2.61	60.5		*ab initio* (pseudopotential)	[41]
	Equilateral	2.52		255	First-principles calculations	[59]
	Equilateral	2.916			MRD CI	[93,147]
	Triangular (C_{2v})	2.62	60.5		First-principles calculations	[95]
	Triangular	2.619	71.0		*ab initio* and par. emp. pot.	[96]
	Equilateral	2.46			DF	[97]
	Triangular (C_{2v})	2.47	63		MD	[98]
	Triangular	2.55	63		MCSCF/MRCI	[137]
	Triangular (D_{3h})	2.569	56.2		MCSCF	[146]
	Triangular (D_{3h})	2.584			Empirical PEF	[149]
	Equilateral (D_{3h})	2.58			MD	[150]
Ni_3	Equilateral	2.21		227.8	DF	This work
				202	Expt.	[27]
	Triangular (C_{2v})		90–100	232.3	Expt.	[103]
	Equilateral	2.5			EH	[24]
	Linear	2.5			MO	[26]
	Linear				ECP-MCSCF-CI	[30]
	Triangular	2.15	61.14		DF	[76]
	Equilateral				CNDO	[92]
	Linear	2.25			MO	[107]
	Triangular (D_{3h})	2.253			Empirical PEF	[149]
	Linear and equilateral				SCF/CCI	[145]
Ti_3	Triangle	2.30	67.97	75.2	DF	This work
	Equilateral	3.1			MO	[26]

we have seen that there was no consensus about the question of whether the considered species is linear, isosceles triangle, or equilateral triangle.

Al_3. With an *ab initio* pseudopotential method, Upton [41] conjectured the triangular form of Al_3 as being most stable. Considering an *ab initio* calculation, Basch [146] found that the Al_3 trimer having lowest energy is in triangular form (nearly equilateral triangle), similarly in his perturbed electron drop model calculation, Upton [95] also obtained the same result. Pettersson *et al.* [96] considered both *ab initio* and parametric empirical potential calculations for Al_n clusters, and they also found that the triangular configuration for Al_3 is energetically most stable. Pacchioni and Koutecký [147] considered pseudopotential calculations and found that linear and equilateral triangle forms of the Al_3 trimer are energetically almost degenerate. On the other hand, Howard *et al.* [148] in their electron-spin-resonance spectroscopy experiment observed that the equilateral triangle geometry of Al_3 has lowest energy. The finding of Tse [137] is the triangular form for Al_3. In his empirical PEF calculation, Erkoç and co-workers [149,150] found the triangular form of Al_3 as most stable. Jones [97], using density-functional calculation, found that the equilateral triangle form of Al_3 is energetically most stable. El-Bayyari and Erkoç [98], using the molecular-dynamics technique, found the triangular form of Al_3 with C_{2v} symmetry as the energetically most stable structure. Finally, with a first-principles calculation, Yang *et al.* [59] found an equilateral triangular structure for the ground state of Al_3. In the present study, we found the ground state to be an equilateral triangle with a bond length of 2.64 Å, which may be seen to be consistent with the other calculations. We also tried a linear geometry for Al_3 and found that its energy is about 0.3 eV greater than that of the equilateral one. We note that our bond length for

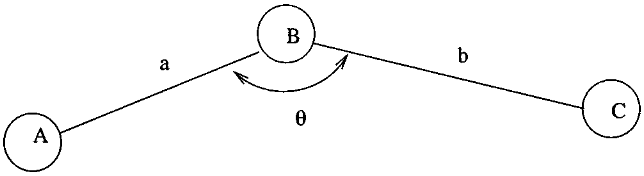

FIG. 1. Geometry of triatom with parameters.

TABLE VI. Trimers of $Al_kTi_lNi_m$ at minimum-energy configurations. Bond lengths a and b are in Å, bond angle θ is in deg, and vibrational frequencies ω_n are in cm^{-1}. The geometry is as shown in Fig. 1. The asterisked frequencies represent the vibrations with maximum amplitude.

A-B-C	a	b	θ	w_1	w_2	w_3	w_4
Al-Al-Al	2.6444	2.6444	60.00	200.7*	201.3	301.1	
Ni-Ni-Ni	2.2184	2.2184	60.00	227.8	231.4*	333.4	
Ti-Ti-Ti	2.3035	2.3035	67.97	75.2*	261.3	368.1	
Al-Ni-Al	2.2907	2.2907	77.87	147.8	302.8*	358.4	
Al-Ni-Ni	2.8152	2.3430	180.00	64.4	75.2	171.4*	245.3
Al-Ti-Al	2.8631	2.8631	64.35	139.0*	182.8	208.4	
Ni-Ti-Ni	2.0346	2.0346	116.81	81.0	340.1	421.5*	
Ti-Ti-Al	2.9985	2.6779	58.56	133.0	203.1*	251.1	
Ti-Ni-Ti	2.3719	2.3719	51.27	143.6	284.7*	470.0	
Ni-Al-Ti	2.3633	2.7302	151.99	45.0	160.9*	351.7	

TABLE VII. Dissociation data of the most stable $Al_kTi_lNi_m$ microclusters: the possible dissociation channels and the corresponding dissociation energies are in eV. The asterisked rows represent the favorable dissociation for the corresponding clusters. Trimer structures are as shown in Fig. 1.

Cluster A-B-C		Dissociation channel	Dissociation energy
Al-Al	→	2Al	−0.4531
Ti-Ti	→	2Ti	−2.8979
Ni-Ni	→	2Ni	−1.2581
Al-Ni	→	Al+Ni	−3.3511
Al-Ti	→	Al+Ti	−2.0708
Ni-Ti	→	Ni+Ti	−2.8032
Al-Al-Al	→	3Al	−2.6859
		Al_2+Al	−2.2328*
Ni-Ni-Ni	→	3Ni	−5.9436
		Ni_2+Ni	−4.6854*
Ti-Ti-Ti	→	3Ti	−5.8400
		Ti_2+Ti	−2.9420*
Al-Ni-Al	→	Al_2+Ni	−4.8000
		2Al+Ni	−5.2531
		AlNi+Al	−1.9020*
Al-Ni-Ni	→	$Al+Ni_2$	−3.6298
		Al+2Ni	−4.8880
		AlNi+Ni	−1.5369*
Al-Ti-Al	→	Al_2+Ti	−3.3556
		2Al+Ti	−3.8087
		Al+AlTi	−1.7379*
Ni-Ti-Ni	→	Ni_2+Ti	−5.7217
		2Ni+Ti	−6.9799
		Ni+NiTi	−4.1766*
Ti-Ti-Al	→	$Al+Ti_2$	−3.0561*
		Al+2Ti	−5.9540
		AlTi+Ti	−3.8832
Ti-Ni-Ti	→	$Ni+Ti_2$	−4.0595*
		Ni+2Ti	−6.9575
		NiTi+Ti	−4.1542
Ni-Al-Ti	→	Al+Ni+Ti	−5.4357
		AlNi+Ti	−2.0846*
		AlTi+Ni	−3.3649
		Al+NiTi	−2.6324

Al_3 is very close to that for the Al_2 dimer (2.6520 Å). Our result for the vibration with the maximum amplitude, $\omega^* = 200.7\ cm^{-1}$, is in reasonable agreement with that of Yang *et al.* [59] ($255\ cm^{-1}$). For a more rigorous treatment of Al_3, see Ref. [146]; and for a detailed information about Al clusters see Ref. [131].

Ni_3. There exists a controversy between theory and experiment for this cluster. With semiempirical methods, Anderson [26,107], and with *ab initio* methods, Basch *et al.* [30] predicted the linear structure to be most stable. Basch *et al.* found that the linear form is more stable by 0.17 eV than the triangular form. In solid argon matrix, Moskovits and DiLella [103] found, on the other hand, the geometry of Ni_3 in solid argon to be a bent structure with an apex angle predicted between 90° and 100°. The semiempirical calculations of Blyholder [92], the extended Hückel calculations of Baetzold [24], and the empirical PEF calculations of Erkoç [149] predicted the equilateral form for Ni_3 as most stable. Blyholder found that the equilateral form was more stable than the linear one by 1.7 eV. Reuse and Khanna [76], with a DFT calculation, found a triangular form with an apex angle 61° being most stable. In this work, we found the ground state to be an equilateral triangle with a bond length of 2.21 Å, which is not too different from the other literature values. Furthermore, our trial linear geometry for Ni_3 has appeared with an energy value that was significantly greater than that of the equilateral one by 3.1 eV. We also note that our bond length of 2.21 Å for Ni_3 is significantly smaller than that for Ni_2 dimer (2.4948 Å). Koutecký and Fantucci [2] state that from theoretical and experimental results the conclusion can be drawn that in a gas phase the Ni_3 species is probably a *fluxional* molecule. As to the vibrational frequency, Moskovits and Hulse [27] attribute a system with a spacing of $202\ cm^{-1}$ to Ni_3. Moskovits and DiLella [103] later observed Ni_3 with a dominant frequency about resonance $232.3\ cm^{-1}$. The present calculated value of $227.8\ cm^{-1}$ is in a good agreement with these two experimental values.

Ti_3. We found the ground state to be a triangle with a bond length of 2.30 Å, an apex angle of 67.97°, and a maximum-amplitude vibration of $75.2\ cm^{-1}$. We have encountered only one theoretical calculation in the literature; Anderson [26], with the molecular-orbital approximation, found the ground state to be an equilateral triangle with a

TABLE VIII. Calculated HOMO, LUMO energies (in hartrees) and HOMO-LUMO gap (E_g) energies (in eV) of dimers and trimers.

Species	HOMO(α)	LUMO(α)	$E_g(\alpha)$	HOMO(β)	LUMO(β)	$E_g(\beta)$
Al-Al	−0.1416	−0.1176	0.6525			
Ni-Ni	−0.1441	−0.1253	0.5124			
Ti-Ti	−0.1118	−0.0776	0.9322			
Al-Ni	−0.1786	−0.0847	2.5556	−0.1744	−0.0922	2.2362
Al-Ti	−0.1643	−0.0765	2.3888	−0.1479	−0.0837	1.7456
Ni-Ti	−0.1191	−0.0821	1.0054			
Al-Al-Al	−0.1714	−0.1162	1.5020	−0.1681	−0.1184	1.3527
Ni-Ni-Ni	−0.1714	−0.0879	2.2718			
Ti-Ti-Ti	−0.1376	−0.0749	1.7039			
Al-Ni-Al	−0.1792	−0.0975	2.2239			
Al-Ni-Ni	−0.1616	−0.0891	1.9736	−0.1607	−0.1499	0.2920
Al-Ti-Al	−0.1466	−0.1128	0.9205	−0.1706	−0.1101	1.6463
Ni-Ti-Ni	−0.1718	−0.0982	2.0046			
Ti-Ti-Al	−0.1607	−0.0715	2.4272	−0.1579	−0.0899	1.8509
Ti-Ni-Ti	−0.1443	−0.0760	1.8580			
Ni-Al-Ti	−0.1909	−0.0996	2.4854	−0.1427	−0.08750	1.5023

bond length of 3.1 Å. We note that the present bond length of 2.30 Å for Ti_3 is greater from that of Ti_2 dimer (1.8537 Å). It is also found that a trial linear geometry for Ti_3 has an energy that is about 2.8 eV above from that of the (isosceles) triangular one.

Heteronuclear trimers. For these species, as well as homonuclear ones discussed above, all the calculated results are given in Table VI. We have encountered neither experimental nor theoretical information about these heteronuclear species in the literature to compare. Data on polyatomic metal clusters was indeed very limited. To the best of our knowledge, the present calculated values are the first for these species. An interesting feature of Table VI is that the optimized minimum energy structure of AlNiNi is linear in the given order. Furthermore, both AlNiNi and TiTiAl trimers have asymmetric structure.

C. Energetics of clusters

We calculated the possible dissociation channels and the corresponding dissociation energies, which are presented in Table VII. It is seen that atomization energies of homonuclear trimers are, not surprisingly, greater than those of the corresponding dimers. Besides, homonuclear trimers X_3 are seen to dissociate as $X_3 \rightarrow X_2 + X$, as expected. All but $X\mathrm{Ti}_2$, all the XY_2 type trimers dissociate as $XY_2 \rightarrow XY + X$. $X\mathrm{Ti}_2$ type trimers, i.e., AlTi_2 and NiTi_2, prefer to fragment into $X\mathrm{Ti}_2 \rightarrow X + \mathrm{Ti}_2$. NiAlTi trimer dissociates as NiAlTi→AlNi + Ti, consistent with the fact that AlNi dimer has the greatest binding energy. For Ni_2 and Ni_3, we found the dissociation energies to be 1.2581 and 4.6854 eV, respectively. These results contradict with the findings of Anderson [107] (using gas-phase UV Ni atom spectra), Lian *et al.* [99] (the collision-induced fragmentation of Ni_n^+ clusters), and Reuse and Khanna [76] (DFT calculations); they all found that the dissociation energy of Ni_3 was lower than that of Ni_2.

We calculated HOMO-LUMO gaps of all the microclusters considered in this work, which are given in Table VIII. The most striking feature is that the calculated HOMO-LUMO energy gaps of dimers are relatively smaller than the corresponding ones for trimers, which may not be expected; but we should not hurry in drawing any conclusion from this result because both homonuclear dimers and the corresponding trimers are too small to be classified as conducting or not. Another feature is that the gaps of α states are relatively larger than that of β states, except AlTiAl trimer.

TABLE IX. Calculated excess charge (in units of electron charge) on atoms and dipole moments (in Debye) of trimers.

A-B-C	$q(A)$	$q(B)$	$q(C)$	μ_x	μ_y	μ
Al-Al-Al	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ni-Ni-Ni	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ti-Ti-Ti	−0.0422	0.0845	−0.0422	0.0727	0.0000	0.0727
Al-Ni-Al	0.3407	−0.6815	0.3407	0.3952	0.0000	0.3952
Al-Ni-Ni	0.2068	0.1295	−0.3362	1.2073	0.0000	1.2073
Al-Ti-Al	0.1308	−0.2616	0.1308	2.0216	0.0000	2.0216
Ni-Ti-Ni	0.1746	−0.3492	0.1746	2.2309	0.0000	2.2309
Ti-Ti-Al	−0.1044	−0.1918	0.2962	2.2304	0.6519	2.3237
Ti-Ni-Ti	0.0274	−0.0548	0.0274	0.1591	0.0000	0.1591
Ni-Al-Ti	−0.3334	0.5133	−0.1800	1.2085	0.0426	1.2092

The calculated excess charge and dipole moments of the trimers are given in Table IX. Because of their rotational symmetry, homonuclear trimers with equilateral-triangular structure, i.e., Al_3 and Ni_3, do not experience charge separations among the atoms, resulting in zero dipole moments. All symmetric trimers, i.e., Ti_3, AlNiAl, AlTiAl, NiTiNi, and TiNiTi, have some excess (positive) charges equally distributed on the end atoms, and the negative charge on the center atom. The remaining trimers, AlNiNi, TiTiAl (which has the largest dipole moment), and NiAlTi, have no symmetry at all, so that their charge separation do not exhibit any regular pattern. We note that all the trimers except Al_3 and Ni_3 bears a net dipole moment, as expected.

In concluding, compared with the experimental and the other theoretical results, the method of calculation and the basis set chosen in the present study are seen to give reliable results for systems considered; therefore, it is quite appropriate to use the same method and basis set for other systems. For example, calculations of larger microclusters of AlTiNi systems may give more interesting results. It is worth working on these binary and ternary metal alloys, especially on their magnetic and optical properties.

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