

Supplementary Material

Anion photoelectron spectroscopy and quantum chemical calculations of bimetallic niobium-aluminum clusters $\text{NbAl}_n^{-/0}$ ($n = 3-12$): Identification of half-encapsulated symmetric structure for NbAl_{12}^-

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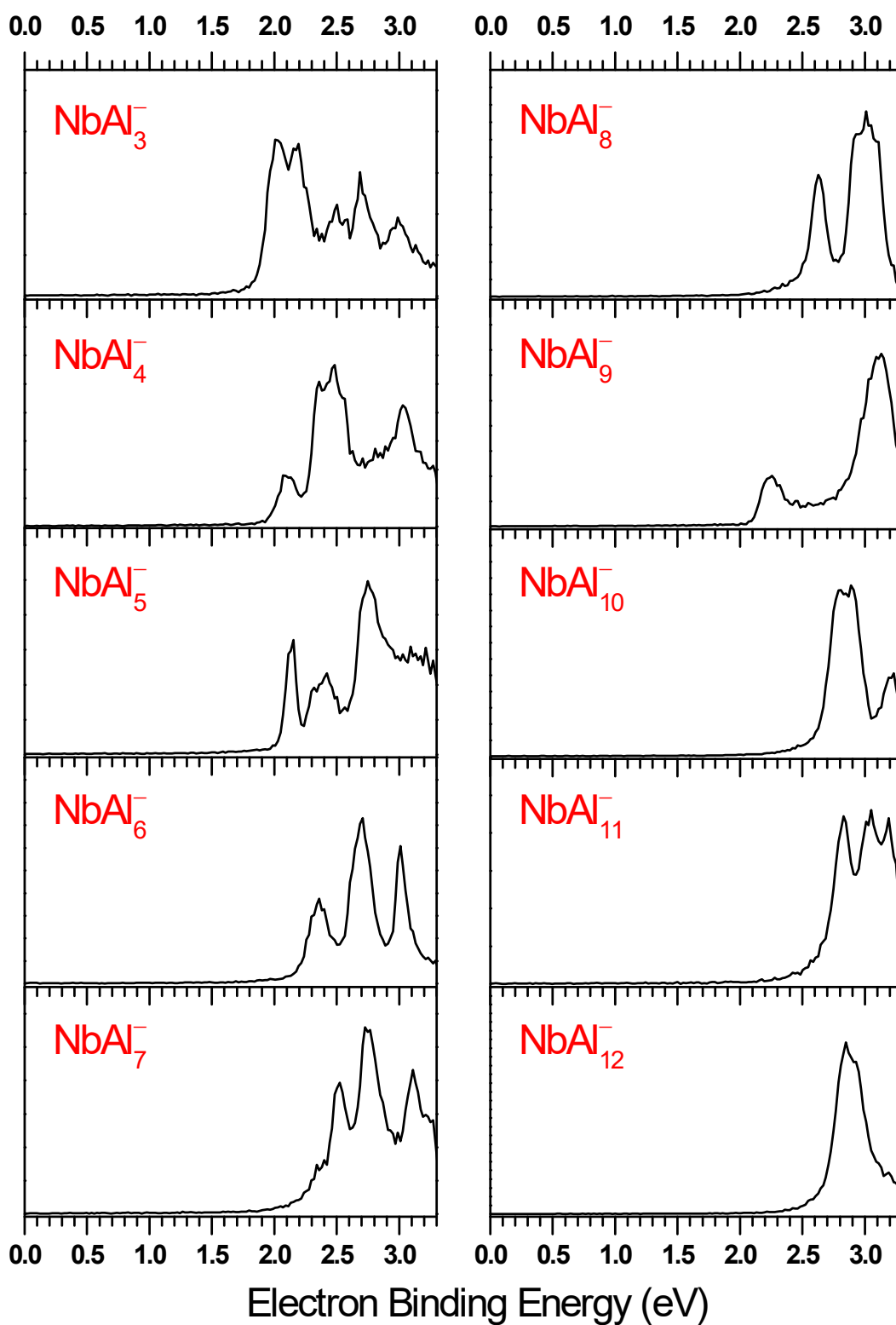


Fig. S1. Photoelectron spectra of NbAl_n^- ($n = 3-12$) clusters recorded with 355 nm photons.

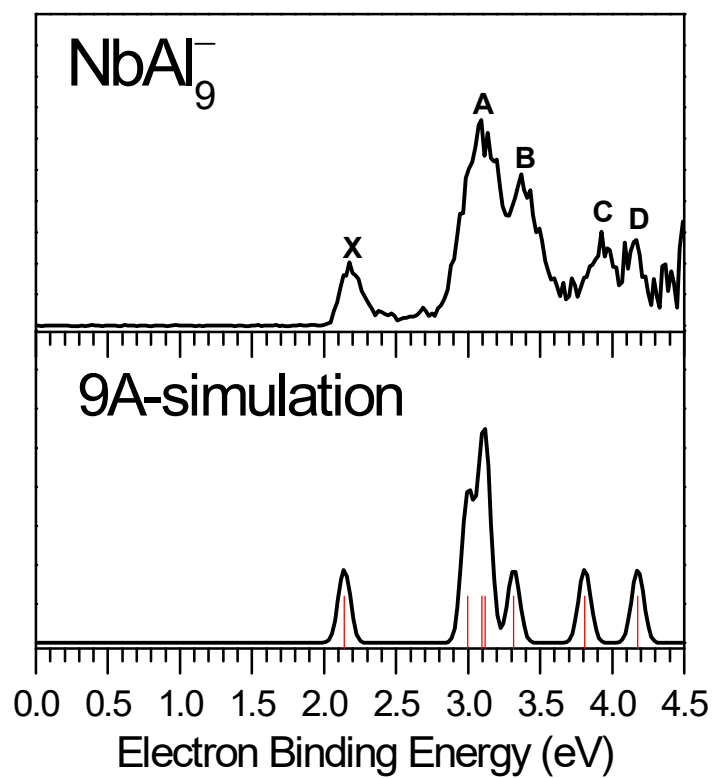


Fig. S2. Comparison between the experimental photoelectron spectrum and the simulated spectrum of the lowest-lying isomer of NbAl₉⁻ (9A) using a combined Δ SCF-TDDFT approach.

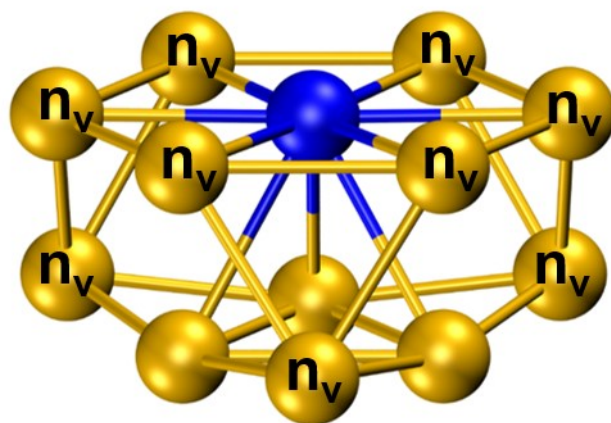


Fig. S3. The most stable structure of NbAl₁₂⁻ (12A) and these obvious vertex atoms are marked as n_v .

Table S1. The average binding energies(E_b), the second order energy difference (Δ_2E) and the splitting energy of Al atom (ΔE_{Al}) values for the most stable isomers of NbAl $_n^{-/0}$ ($n = 3-12$) clusters.

Number of Al atoms, n	E_b /eV		Δ_2E /eV		ΔE_{Al} /eV	
	anionic	neutral	anionic	neutral	anionic	neutral
3	2.35	2.02	---	---	---	---
4	2.53	2.25	0.75	0.79	3.26	3.15
5	2.53	2.27	-0.99	-1.04	2.51	2.36
6	2.67	2.43	0.81	0.69	3.50	3.40
7	2.67	2.46	-0.10	0.24	2.69	2.70
8	2.69	2.46	-0.54	-1.23	2.80	2.47
9	2.75	2.59	0.22	1.04	3.34	3.70
10	2.78	2.59	0.40	-0.13	3.12	2.66
11	2.78	2.61	-0.81	-0.60	2.72	2.79
12	2.84	2.67	---	---	3.53	3.38

Table S2. Cartesian coordinates for stable isomers of NbAl_n^- ($n = 3-12$) clusters.

NbAl_3^-							
3A			3B				
	X	Y	Z		X	Y	Z
Nb	-0.96928700	-0.00078900	0.06881100	Nb	-0.00000000	-0.00000000	0.71880600
Al	0.92229500	-1.54049000	-0.80113700	Al	0.00000000	0.00000000	-1.73997800
Al	1.21599100	0.00284200	1.38788800	Al	0.00000000	2.35348400	-0.26351200
Al	0.91869700	1.54013700	-0.80377000	Al	-0.00000000	-2.35348400	-0.26351200
3C							
	X	Y	Z		X	Y	Z
Nb	-1.40092700	0.00000600	-0.00001100				
Al	2.93063600	0.00000400	-0.00003300				
Al	0.74384700	1.39122800	0.00003300				
Al	0.74382500	-1.39125100	0.00003300				
NbAl_4^-							
4A			4B				
	X	Y	Z		X	Y	Z
Nb	0.00125200	-0.91207000	0.00028000	Nb	0.00007900	-0.46426700	-0.00008800
Al	2.27192200	0.38838500	0.00009100	Al	-1.51619000	1.60346800	-0.00010100
Al	-0.00117000	1.05083700	-1.55837800	Al	1.51580800	1.60377000	0.00014600
Al	-0.00145200	1.05194400	1.55750700	Al	2.53258400	-0.87142900	0.00004200
Al	-2.27324700	0.38536200	-0.00010200	Al	-2.53245000	-0.87158200	0.00019000
4C							
	X	Y	Z		X	Y	Z
Al	0.61426400	1.59397700	-0.59901500				
Al	0.41847200	-0.00094300	1.65721800				
Al	0.61365100	-1.59313400	-0.60031200				
Al	2.64251200	-0.00024100	-0.14487500				
Nb	-1.35989500	0.00010800	-0.09924900				

NbAl₅⁻

5A			5B				
	X	Y	Z	X	Y	Z	
Al	-0.21723900	0.97929000	-1.39865400	Al	-1.31269900	1.69636100	-0.13942200
Nb	0.83994200	-0.91103600	-0.00017300	Nb	-0.00011900	-0.53868800	-0.62254700
Al	-2.55579500	0.99209100	-0.00001200	Al	1.31285800	1.69642300	-0.13891300
Al	2.05597900	1.38944700	-0.00016900	Al	-2.50041900	-0.77181000	0.20064800
Al	-0.21618800	0.97922900	1.39902100	Al	0.00026600	-0.15000300	1.84100000
Al	-1.71580400	-1.46679000	0.00035800	Al	2.50037100	-0.77203100	0.20010300

5C			
	X	Y	Z
Al	0.52293800	0.00054000	-1.26567300
Nb	-1.81129400	0.00032000	-0.12631300
Al	0.03397800	-1.55566000	0.85419800
Al	2.56049900	1.31049400	-0.02365200
Al	2.56008500	-1.31073100	-0.02272200
Al	0.03504300	1.55434700	0.85622200

NbAl₆⁻

6A			6B				
	X	Y	Z	X	Y	Z	
Nb	-1.63568000	-0.00056800	0.00014000	Nb	-1.07973000	-0.02426000	-0.41808500
Al	0.45168100	-0.00003500	-1.44802300	Al	-1.03605100	2.35283800	0.62174300
Al	2.36986100	1.31229700	-0.00010800	Al	0.50754200	0.01004300	1.61662200
Al	-0.24405000	2.22255500	-0.00067000	Al	0.99683900	1.48419000	-0.92860900
Al	2.37136500	-1.31073200	0.00027500	Al	1.06240600	-1.43618400	-0.93221100
Al	-0.24175900	-2.22302100	-0.00039900	Al	-0.92690200	-2.39674300	0.62232600
Al	0.45158400	0.00072800	1.44848300	Al	2.80146900	0.06236600	0.31870600

6C			
	X	Y	Z
Nb	-0.62313800	-0.90784600	-0.22435400
Al	-1.56617800	1.24214100	-1.24756700
Al	1.71520700	-1.37866800	0.74643000
Al	-2.35037500	0.39291100	1.35573800
Al	0.18033300	1.31615400	0.92918900
Al	2.73071300	1.07891600	0.47120300
Al	1.25558200	0.21175200	-1.54741300

NbAl₇⁻

7A				7B			
	X	Y	Z		X	Y	Z
Nb	1.28243100	-0.69860900	-0.41514200	Al	1.85506400	2.29842000	-0.06651700
Al	-0.34401900	0.40488700	1.34502200	Al	-1.56684000	0.56311500	1.67862100
Al	-0.74646400	-2.18413700	0.50001400	Al	1.74515300	-2.16320300	0.35851800
Al	-1.05384500	-0.33504800	-1.47430200	Al	-2.88787300	0.09781500	-0.70167400
Al	0.63871800	1.81106700	-0.89433700	Al	1.75661400	-0.02149600	-1.33124200
Al	-1.92631200	1.89579400	-0.19033800	Al	1.13880600	0.35712100	1.48854000
Al	-2.86008200	-0.41193300	0.66199100	Al	-0.58767000	1.68854100	-0.69065400
Al	2.24741200	1.02267700	1.36124300	Nb	-0.46078900	-0.89424600	-0.23323700

7C			
	X	Y	Z
Nb	1.89120500	-0.00110400	-0.35240000
Al	0.27503400	0.00016300	1.66303700
Al	-1.84878200	-1.36148700	0.77439000
Al	-1.84590500	1.36494400	0.77169100
Al	0.61537000	-2.22149100	0.13731700
Al	0.61939300	2.22151900	0.13700200
Al	-0.50407700	-0.00017600	-1.24064900
Al	-3.27560100	0.00001100	-1.13137300

NbAl₈⁻

8A				8B			
	X	Y	Z		X	Y	Z
Nb	1.42683100	0.00171200	-0.00009700	Nb	-0.86407300	0.92274400	0.00007400
Al	-0.17142400	-1.77190900	-1.29229400	Al	-1.08855800	-1.30417700	-1.42070800
Al	-2.73327900	0.99467400	0.81399300	Al	1.22996700	0.10244800	-1.41727000
Al	-2.72700000	-1.00123000	-0.81524000	Al	1.28623100	2.41703300	-0.00026700
Al	-0.78578800	0.81677200	-1.16372400	Al	1.23016800	0.10308200	1.41723400
Al	1.44353300	-2.49076300	0.86419000	Al	-3.24118700	-0.15197200	-0.00003700
Al	-0.17897300	1.76968100	1.29205600	Al	0.96796800	-2.16482700	0.00023500
Al	-0.78500300	-0.81829000	1.16213600	Al	-1.08837300	-1.30421700	1.42068000
Al	1.43792900	2.49566600	-0.86081300	Al	3.42893800	-0.60756200	-0.00009900
8C							
	X	Y	Z		X	Y	Z
Al	-0.11005400	-1.43670100	1.62632700				
Al	-1.45049300	-2.60400700	-0.42145400				
Al	-1.45051100	2.60399000	-0.42149300				
Al	3.23220300	-0.00001400	-0.98228000				
Nb	-1.28616100	-0.00001200	-0.29344000				
Al	-0.11009100	1.43673200	1.62630300				
Al	0.95221600	-1.33654300	-0.98485200				
Al	2.04087300	0.00004500	1.46778000				
Al	0.95220900	1.33653500	-0.98486700				

NbAl₉⁻

9A			9B				
	X	Y	Z		X	Y	Z
Nb	-0.00027600	-0.00111400	-1.23645000	Al	0.70362600	-1.33442900	-1.41254800
Al	0.78155800	2.51194300	-0.61204000	Al	0.69674600	1.34208200	-1.41242200
Al	1.78618500	-1.93395300	-0.60932300	Nb	-1.49298800	-0.00164900	-0.89379000
Al	2.34680700	0.52989100	0.14298700	Al	-0.81396700	-2.25363700	0.78260200
Al	-1.63189000	1.76665700	0.14278800	Al	1.86206600	-2.42529800	0.71121900
Al	0.47310800	1.52245500	1.76599500	Al	0.54480700	0.00086200	1.12229700
Al	-0.71383300	-2.29585500	0.14631300	Al	1.85049200	2.43025000	0.71633900
Al	1.08053700	-1.16780900	1.76680100	Al	-0.82732900	2.24712300	0.78742700
Al	-2.56784400	-0.58044200	-0.61055400	Al	-2.13258800	-0.00891600	1.71628800
Al	-1.55375900	-0.34937200	1.76660700	Al	2.82480000	0.00716300	-0.19232600

9C			
	X	Y	Z
Al	-0.01828100	1.37438700	-1.15333900
Al	1.24970700	2.80047100	0.89615100
Al	-1.09500600	-1.48759900	1.36900200
Al	2.64790600	1.32923300	-0.77547700
Al	2.64243700	-1.33357600	-0.77942300
Al	1.24496900	-2.80170300	0.89715800
Al	-0.02360700	-1.37724000	-1.15164800
Al	-1.09039600	1.48904500	1.36825700
Al	1.10703000	-0.00169100	1.05630100
Nb	-2.11321700	0.00275000	-0.54758000

NbAl₁₀⁻

10A			10B				
	X	Y	Z	X	Y	Z	
Nb	-0.00003600	-0.00246100	-1.15698500	Al	-2.67206900	-0.22234200	-1.33832400
Al	-1.34707800	-2.10023100	-0.09973200	Al	1.03313900	2.56195700	0.81637800
Al	2.71944700	-0.00206600	-1.25343200	Al	-1.04563300	1.89661400	-0.64345500
Al	1.34865700	-2.09980300	-0.09990000	Al	-2.77281200	0.66694100	1.14911900
Al	-1.34877200	2.09859000	-0.10885000	Al	-1.63051700	-1.73263900	0.88722600
Al	-0.00065100	1.32400300	1.96402600	Al	1.82057200	1.25161100	-1.25599300
Al	-2.26052500	0.00197000	1.32013800	Al	2.30038600	0.22935500	1.35320500
Al	0.00077200	-1.31375700	1.96853000	Al	2.56935000	-1.25309500	-0.76797100
Al	-2.71969700	-0.00350000	-1.25316200	Al	-0.31520100	0.40438600	1.75984300
Al	1.34719100	2.09912200	-0.10866300	Nb	-0.04777200	-0.55353000	-1.02113500
Al	2.26077100	0.00343600	1.31999800	Al	0.86345100	-2.05703900	1.26047600

10C			
	X	Y	Z
Nb	-0.12240600	-0.34923500	-1.11998900
Al	-0.10608600	1.12272500	1.53841200
Al	0.90437600	2.11531200	-0.90925200
Al	-2.77082500	-0.61931500	-0.94383400
Al	-1.09609000	-1.59224200	1.19584600
Al	1.02725400	-2.48124800	-0.09269700
Al	1.64248000	-0.84252500	1.74265900
Al	2.54154300	-0.32937100	-1.01967300
Al	-1.70336600	1.84669600	-0.45094400
Al	-2.63669100	0.44732700	1.54796800
Al	2.58345600	1.43407400	0.92378800

NbAl₁₁⁻

11A			11B				
	X	Y	Z	X	Y	Z	
Nb	-0.03013900	-0.07464200	-1.02621900	Nb	-0.13164800	0.25129600	-0.95009500
Al	-0.87560300	0.95576400	1.65931400	Al	1.61527900	-1.69881000	-1.39762500
Al	2.23579500	-1.34287500	-1.26251700	Al	-1.17273700	0.82319000	1.66754800
Al	-0.45688000	-1.81788400	1.06110400	Al	-1.95681900	2.24799700	-0.58208300
Al	-2.52817000	0.98264400	-0.63908800	Al	0.42519200	-1.48994200	1.26569500
Al	2.13874600	1.46674500	-0.93598300	Al	-1.04828100	-2.33957300	-0.91232200
Al	-2.10076800	-1.73837700	-1.15220300	Al	1.48483400	0.91235900	1.87670800
Al	-2.81395000	-0.72059600	1.31794700	Al	2.95016500	-1.00960200	0.78454900
Al	1.67210100	-0.04475100	1.35872300	Al	-2.75972400	-0.24889500	-0.54243500
Al	2.03229400	-2.57816400	1.01652600	Al	0.55891400	2.68854400	0.17173100
Al	-0.47917900	2.55010500	-0.55240300	Al	-2.11370900	-1.64469300	1.56750900
Al	1.27066700	2.52279800	1.36511700	Al	2.43208300	0.96687600	-0.90282200
11C							
	X	Y	Z				
Al	2.36021100	1.91881800	0.66295400				
Al	2.19179000	0.36956400	-1.43846700				
Al	1.19974800	-2.04212100	-0.95288000				
Al	-0.07572600	-2.21311400	1.38628000				
Al	2.48824600	-0.90196800	1.04970600				
Al	-2.06018700	2.03164900	0.85699300				
Al	-0.04149600	1.96139300	-1.20367500				
Al	-2.33842000	-0.69693000	1.26273000				
Al	-1.50228600	-1.95987600	-0.84270200				
Al	-0.16292400	-0.29225600	-2.38158400				
Al	-2.39470900	0.54414300	-1.22678100				
Nb	0.10645900	0.40607500	0.89650100				

NbAl₁₂⁻

12A

	X	Y	Z
Al	1.55868500	-0.33881600	1.51873100
Al	-1.07267700	-1.17952600	1.51880200
Al	2.59523400	0.79666700	-0.91262900
Al	-1.99057300	1.84790100	-0.91331000
Nb	-0.00206100	0.00006600	-0.87826800
Al	-0.48345900	1.52088200	1.51907300
Al	2.03243700	2.23069100	1.22575900
Al	0.55087800	2.65526000	-0.91330300
Al	-2.57915200	-0.85403000	-0.90730100
Al	-2.94375100	0.64471800	1.23013800
Al	-0.60471800	-2.64570400	-0.91430700
Al	2.02734800	-1.80517100	-0.90935000
Al	0.91624600	-2.87308300	1.22761800

12B

	X	Y	Z
Al	0.47507700	-1.79389100	-1.75118500
Al	-3.47631000	-0.09943700	0.25047100
Al	-1.50088000	0.70852000	1.73846700
Al	2.19381600	2.26332400	0.08831000
Nb	0.15502900	0.65344700	-0.53680600
Al	0.35776400	-1.14738000	2.37675600
Al	1.07270800	1.33630000	2.20580900
Al	-1.92022600	-0.43509100	-1.90256900
Al	2.42514400	0.32197600	-2.00348400
Al	2.33283000	-0.64840900	0.46033400
Al	-1.37538000	-1.69931300	0.44094000
Al	1.00172000	-2.91813500	0.47597000
Al	-2.07520300	2.05066400	-0.68681500

12C

	X	Y	Z
Al	-2.43501000	2.25711900	0.54135600
Al	-1.44127800	0.00114900	1.60780000
Al	0.08864900	-2.08756500	1.41722700
Al	1.54555500	-0.00049500	1.79755200
Nb	0.05184600	0.00046600	-0.96065700
Al	2.03009200	-1.68720500	-0.55508200
Al	3.83851300	-0.00285700	0.20208500
Al	-0.45380500	2.57668800	-1.21517200
Al	2.03276800	1.68490100	-0.55424000
Al	0.09012500	2.08792400	1.41763300
Al	-2.56511500	-0.00081700	-0.95677300
Al	-0.45801700	-2.57481100	-1.21610200
Al	-2.43599200	-2.25550100	0.54348100