



AFRL-AFOSR-VA-TR-2016-0081

**CLUSTER DYNAMICS: LAYING THE FOUNDATION FOR
TAILORING THE DESIGN OF CLUSTER ASSE**

**Albert Castleman
PENNSYLVANIA STATE UNIVERSITY
201 OLD MAIN
UNIVERSITY PARK, PA 16802-1505**

**02/25/2016
Final Report**

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/RTB2

Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE			<i>Form Approved</i> OMB No. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services, Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.</p>					
1. REPORT DATE (DD-MM-YYYY) 25-02-2016		2. REPORT TYPE Final Performance		3. DATES COVERED (From - To) 15-04-2010 to 15-10-2015	
4. TITLE AND SUBTITLE CLUSTER DYNAMICS: LAYING THE FOUNDATION FOR TAILORING THE DESIGN OF CLUSTER ASSEMBLED NANOSCALE MATERIALS				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-10-1-0071	
				5c. PROGRAM ELEMENT NUMBER 61102F	
6. AUTHOR(S) Albert Castleman				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) PENNSYLVANIA STATE UNIVERSITY 201 OLD MAIN UNIVERSITY PARK, PA 16802-1505 US				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR RTB2	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT A DISTRIBUTION UNLIMITED: PB Public Release					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Our overall goal is to establish the groundwork for using clusters as the building blocks of new materials with tailored properties that are beneficial to the AFOSR. Our continuing program is composed of two interrelated themes: the first comprises the investigation of fundamental physical and chemical properties of cluster building blocks in isolation, while the second involves the study of cluster deposition and assembly, including optical and chemical characterization of the formed materials. The ability to tune the pertinent properties of matter would facilitate the design of devices that could behave ideally in a specific application. Our objectives are outlined as follows: 1. Explore the electronic and geometric structure of clusters to enable the design of stable motifs for use in high energy-density materials and nanocatalysis. 2. Characterize dynamical processes to allow the precise control of building block reactivity on the atomic scale. 3. Extend the formalism for describing the interactions of clusters in rarefied environments to build a methodology for treating deposited clusters. 4. Examine the intra and inter cluster length scale interactions of deposited clusters to determine how the properties of the nanoscale material emerge.					
15. SUBJECT TERMS CLUSTER, FOUNDATION					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF	19a. NAME OF RESPONSIBLE PERSON Albert Castleman
a. REPORT	b. ABSTRACT	c. THIS PAGE			
Standard Form 298 (Rev. 8/98) Prescribed by ANSI Std. Z39.18					

Unclassified	Unclassified	Unclassified	UU	PAGES	19b. TELEPHONE NUMBER <i>(Include area code)</i> 814-865-7242
--------------	--------------	--------------	----	--------------	---

To: technicalreports@afosr.af.mil

Subject: Final Report Statement to Dr. Michael Berman

Contract/Grant Title: Cluster Dynamics: Laying the Foundation for Tailoring the Design of Cluster Assembled Nanoscale Materials

Contract/Grant #: FA9550-10-1-0071, P01

Reporting Period: April 15, 2014 – October 14, 2015

Final Accomplishments:

In order to understand the foundation for tailoring the design of cluster assembled materials, our research continues to investigate the electronic structures of small metal clusters and metalloids, and their role in cluster stability, reactivity, and mimicry. The final reporting period was focused on the rare earth mimicry and the properties of clusters containing Al, B, and Ag elements.

As an extension of our superatom concept, in the last year we have shown evidence in rare earth mimicry. We provided direct experimental evidence that the neutral LaB and NdB clusters have similar unpaired electrons and magnetic moments as their isovalent Nd and Eu rare earth elements, respectively. Extension of the superatom concept into the rare earth group will be of great importance in designing novel building blocks in the application of cluster-assembled nanomaterials. Additionally, a new experimental strategy is proposed to significantly increase the yield of the rare earth anions, providing the best opportunity to complete the periodic table of the atomic anions.

Other reactivity work has focus on the energetic aluminum boride clusters. The $Al_{12}B^-$ and $Al_{11}B_2^-$ clusters are found to be resistant to reactivity with O_2 due to their closed electronic shell, making them potential candidates to form cluster assembled solids. Other detailed studies were conducted during the past year have led to the discovery of C-S bond activation in the reaction of silver cluster anions with ethanethiol, which may offer insight into the mechanism by which ligand-protected clusters could be synthesized.

Publications During Current Grant Period:

*Publication in press after the April 2013-2014 progress report, listed here for final citation.

- *707. “Photoelectron Imaging Spectroscopy of NbN⁻: Exploring Similarities with its Isovalent Analogues ZrO⁻ and Pd⁻”, C. Berkdemir, K. D. D. Gunaratne, S. Cheng and A. W. Castleman, Jr., *Physical Chemistry Chemical Physics*, (submitted 2013).
- *711. “Assigning the Mass Spectrum of NbN⁻: Photoelectron Imaging Spectroscopy and Nominal-mass Counterpart Analysis.” C. Berkdemir, S.B. Cheng and A.W. Castleman, Jr., *Int. J. Mass spectrom.*, **365-366** 222-224 (2014).
712. “Reactivity of Silver Clusters Anions with Ethanethiol”, Z. Luo, G. U. Gamboa, M. Jia, A. C. Reber, S. N. Khanna and A.W. Castleman, Jr., *Journal of Physical Chemistry Special Issue A. W. Castleman, Jr. Festschrift*, **118**, 8345-8350 (2014).
713. “Special and General Superatoms”, Z. Luo and A.W. Castleman, Jr., *Acc. Chem. Res.*, **47**, 2931-2940 (2014).
714. “Boron Substitution in Aluminum Cluster Anions: Magic Clusters and Reactivity with Oxygen”, J. Smith, A. Reber, S. Khanna and A.W. Castleman, Jr., *Journal of Physical Chemistry Special Issue A. W. Castleman, Jr. Festschrift*, **118**, 8485-8492 (2014).
715. “Direct Experimental Observation of Weakly-Bound Character of the Attached Electron in Europium Anion”, Shi-Bo Cheng and A.W. Castleman, Jr., *Scientific Reports*, **5** 12414 (2015).
716. “Mass Spectrometry and Its Role in Advancing cluster Science”, P. Jena and A.W. Castleman, Jr., *IJMS*, **377**, 235-247 (2015).
717. “Joint Photoelectron Imaging Spectroscopic and Theoretical Characterization on the Electronic Structures of the Anionic and neutral ZrC₂ Clusters”, Shi-Bo Cheng and A. W. Castleman, Jr., *J. Phys. Chem. A*, **118**, 6935-6939 (2014).
718. “Mimicking the magnetic properties of rare earth elements using superatoms”, Shi-Bo Cheng, C. Berkdemir and A. W. Castleman, Jr., *PNAS*, **112**, 4941-4945 (2015).
719. “On the Electronic Structure of the Diatomic VO anion: A Combined Photoelectron Imaging Spectroscopic and Theoretical Investigation”, Shi-Bo Cheng, C. L. Harmon and A. W. Castleman, Jr., *J. Phys. Chem. A.*, (submitted 2015).

Changes in research objectives, if any: None

Change in AFOSR program manager, if any: None

Extensions granted or milestones slipped, if any: None

New discoveries, inventions, or patent disclosures during this reporting period: None

1.

1. Report Type

Final Report

Primary Contact E-mail

Contact email if there is a problem with the report.

cmf11@psu.edu

Primary Contact Phone Number

Contact phone number if there is a problem with the report

814-863-0119

Organization / Institution name

Penn State University

Grant/Contract Title

The full title of the funded effort.

Cluster Dynamics: Laying the Foundation for Tailoring the Design of Cluster Assembled Nanoscale Materials

Grant/Contract Number

AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-10-1-0071

Principal Investigator Name

The full name of the principal investigator on the grant or contract.

A. Welford Castleman, Jr.

Program Manager

The AFOSR Program Manager currently assigned to the award

Michael Berman

Reporting Period Start Date

04/15/2010

Reporting Period End Date

10/14/2015

Abstract

Our overall goal is to establish the groundwork for using clusters as the building blocks of new materials with tailored properties that are beneficial to the AFOSR. Our continuing program is composed of two interrelated themes: the first comprises the investigation of fundamental physical and chemical properties of cluster building blocks in isolation, while the second involves the study of cluster deposition and assembly, including optical and chemical characterization of the formed materials. The ability to tune the pertinent properties of matter would facilitate the design of devices that could behave ideally in a specific application. Our objectives are outlined as follows: 1. Explore the electronic and geometric structure of clusters to enable the design of stable motifs for use in high energy-density materials and nanocatalysis. 2. Characterize dynamical processes to allow the precise control of building block reactivity on the atomic scale. 3. Extend the formalism for describing the interactions of clusters in rarefied environments to build a methodology for treating deposited clusters. 4. Examine the intra and inter cluster length scale interactions of deposited clusters to determine how the properties of the nanoscale material emerge.

Distribution Statement

This is block 12 on the SF298 form.

Distribution A - Approved for Public Release

Explanation for Distribution Statement

If this is not approved for public release, please provide a short explanation. E.g., contains proprietary information.

SF298 Form

Please attach your [SF298](#) form. A blank SF298 can be found [here](#). Please do not password protect or secure the PDF. The maximum file size for an SF298 is 50MB.

[Castleman AFOSR Final Report Cover.pdf](#)

Upload the Report Document. File must be a PDF. Please do not password protect or secure the PDF. The maximum file size for the Report Document is 50MB.

[AFOSR Final Report 2016 done 2-3-16.pdf](#)

Upload a Report Document, if any. The maximum file size for the Report Document is 50MB.

Archival Publications (published) during reporting period:

Changes in research objectives (if any):

Change in AFOSR Program Manager, if any:

Extensions granted or milestones slipped, if any:

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, \$K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

Report Document - Text Analysis

Appendix Documents

2. Thank You

E-mail user

Feb 17, 2016 10:22:23 Success: Email Sent to: cmf11@psu.edu