FINAL TECHNICAL REPORT

THEORETICAL STUDIES ON THE ELECTRONIC STRUCTURES AND
PROPERTIES OF COMPLEX CERAMIC CRYSTALS AND NOVEL MATERIALS

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Abstract

This project is a continuation of a long program supported by the Office of Basic Energy Science in the Office of Science of DOE for many years. The final three-year continuation started on November 1, 2005 with additional 1 year extension to October 30, 2009. The project was then granted a two-year No Cost Extension which officially ended on October 30, 2011. This report covers the activities within this six year period with emphasis on the work completed within the last 3 years. A total of 44 papers with acknowledgement to this grant were published or submitted. The overall objectives of this project are as follows. These objectives have been evolved over the six year period:

- (1) To use the state-of-the-art computational methods to investigate the electronic structures of complex ceramics and other novel crystals.
- (2) To further investigate the defects, surfaces/interfaces and microstructures in complex materials using large scale modeling.
- (3) To extend the study on ceramic materials to more complex bioceramic crystals.
- (4) To initiate the study on soft condensed matters including water and biomolecules.
- (5) To focus on the spectroscopic studies of different materials especially on the ELNES and XANES spectral calculations and their applications related to experimental techniques.
- (6) To develop and refine computational methods to be effectively executed on DOE supercomputers.
- (7) To evaluate mechanical properties of different crystals and those containing defects and relate them to the fundamental electronic structures.
- (8) To promote and publicize the first-principles OLCAO method developed by the PI (under DOE support for many years) for applications to large complex material systems.
- (9) To train a new generation of graduate students and postdoctoral fellows in modern computational materials science and condensed matter physics.
- (10) To establish effective international and domestic collaborations with both experimentalists and theorists in materials research.

Because of the large amount of work accomplished, a diverse class of materials covered and the desire for an easier reporting process, this report will list six categories (A to F) of major accomplishments and findings under the following headings with references to the published papers under DOE support. These six categories obviously have heavy overlaps. A complete list of published papers follows the brief description on each category. Each paper also indicates to which of the six categories the main accomplishment it belongs to.

- A. Electronic structure of complex and novel crystals
- B. Impurities, surfaces, interfaces and microstructures in ceramics
- C. Structures and properties of complex bioceramics
- D. Soft condensed matters
- E. Spectroscopic characterizations, XANES and ELNES spectroscopy
- F. Large-scale simulations

Technical Report

This technical report describes the six categories of accomplishments. Only two of the most significant ones (with * on the list) are described under each category. Others will be referred to the published papers listed at the end. The PDFs of these papers will be provided upon request. Most of the paper falls under A (34 papers) and followed by E (31 papers) which is consistent with the main goal of the project. Categories B and F each listed 12 papers and followed by D (7 papers) and C (3 papers).

A. Electronic structure of complex and novel crystals

(1-3, 4,6, 8-13, 15-21, 23-26, 28*, 30-33, 39*, 37-40, 42-44. Total: 34 papers)

Paper [28] reports a theoretical study of the large linear dichroism of herapathite. Herapathite is a crystal of long historical interest originally discovered 150 years ago. It has strong optical anisotropy that has intrigued scientists for a long time. There were no theoretical calculations of its electronic structure and optical properties because its crystal structure is unknown until recently. In this paper, we reported the *ab initio* calculation of the electronic structure and optical properties of this extremely complicated crystal, thereby explaining the origin of its intense optical anisotropy. Current molecular orbital theory on triiodide molecule in gaseous phase or in simple alkali iodides is not adequate to explain the electronic structure in herapathite.

Paper [39] is a recent publication. Iota-alumina (ι -Al₂O₃) is a mullite like phase of alumina that was first reported more than 50 years ago but its structure has evaded detection for a long time. We have successfully determined the structure of ι -Al₂O₃ starting from the experimental structural data of a high alumina content mullite phase. Simulated x-ray diffraction pattern agrees well with measured ones. Based on this theoretically constructed model, we calculated a wide range of its physical properties including elastic, thermodynamic, electronic and spectroscopic properties. We showed that ι -Al₂O₃ may be a hitherto unknown ultra-low density transition phase preceding γ -Al₂O₃ in the processing to stable alumina.

B. Impurities, surfaces, interfaces and microstructures in ceramics

(1,5,8,10,14*,18,22,27,29,32*,35,36. Total: 12 papers)

Paper [14] reports a detailed calculation on the electronic structure, bonding, charge distribution and X-ray absorption spectra of the (001) surfaces of two important bioceramic crystals, fluorapatite (FAP) and hydroxyapatite (HAP). In both crystals, the O-terminated (001) surface is more stable with calculated surface energies of 0.865 J/m² and 0.871 J/m² for FAP and HAP respectively. The largest relaxations occurred *via* the lateral movements of the O ions at the sub-surface level. The electronic structures of the surface models are presented in the form of layer-by-layer resolved partial density of states, Mulliken effective charges and bond order values between cations (Ca, P) and anions (O, F) showing different charge transfers and bond strength variations from bulk crystal values. Electron charge density calculations show these surfaces are mostly positively charged due to the presence of Ca ions at the surface. The XANES spectra (Ca-K, O-K, F-K, P-K, and P-L₃ edges) of both the surface models and bulk crystals are calculated and compared. This work leads to further studies on complex bioceramics crystals.

Paper [32] reports a comprehensive study of the physical properties of a prismatic model of intergranular glassy film (IGF) in silicon nitride using large-scale *ab initio* simulation. The model with 907 atoms is an extension of earlier work (under DOE support) on a smaller basal IGF model. The work reported is among the most realistic description of this microstructure in structural ceramics and these calculations are the first time results giving tremendous insights on the nature of mechanical deformation of this common microstructure in structure ceramics. More importantly, it makes a connection between the mechanical and elastic behavior to fundamental electronic structure and bonding in these materials.

C. Structures and properties of complex bioceramics

(14, 24*, 29*. Total: 3 papers)

Paper [24] reports highly accurate calculations on the elastic and bulk properties of hydroxyapatite using *ab initio* methods based on density functional theory. The results show good agreement with most of the quoted experimental values. We then investigated the failure mechanism in this crystal by performing theoretical tensile experiments which are very difficult to conduct experimentally. Our results show anisotropic behavior in the stress-strain relationship of the apatite crystal which has important implications on the mineralization of bone tissues and dentin materials. This work also leads to the new concept of constructing failure envelope of a material using multi-axial simulation data which is currently in progress.

Paper [29] reports the results of a comprehensive study of the mechanical properties, electronic structure and bonding of α - and β -tri-calcium phosphates with surface characterization. This work follows earlier study on HAP and FAP bioceramics crystals (see B-[14*] above). These two crystals have extremely complicated crystal structures and high precision calculations for such systems are very rare. This is also the first time the mechanical properties on these two important bioceramic crystals were reported. In particular, we were able to link the differences in the mechanical properties in these two TCP polymorphs to their fundamental electronic structure and bonding. In addition, we reported the surface structure and surface charge distribution of these two crystals which have implications on bioactivities related to these two crystals.

D. Soft condensed matters

(7, 21, 23, 28, 30*, 34*, 41. Total: 7 papers)

Paper [30] is the report of a workshop organized by Roger French and V. Adrian Parsegian under the sponsorship of the Office of Basic Energy Sciences at DOE to assess the broad area of long-range interactions in nanoscale science. It involves many active researchers working on various aspects of the long-range interactions both experimentally and theoretically. Our contribution to this paper is in demonstrating the possibility of using calculated optical spectra as input to evaluate the long-range Van der Waals interactions. We used a periodic model of a double strand DNA molecule as an example. The anisotropic optical properties of the DNA will have profound implications on the directionally dependent long range interactions.

Paper [34] reports an *Ab initio* investigation of hydrogen bonding and network structure in a supercooled model of water. Water is a ubiquitous substance of critical interest to an array of

diverse fields especially in biomolecular systems. This work clarified many subtle points regarding the nature of the network structure by quantitatively and concisely defining hydrogen bonding in water based on quantum mechanically calculated bond order values. It provided a detailed statistical analysis that reflects the relationship between hydrogen bonding and local atomic configurations in bulk water. We have correctly reproduced the experimentally observed features of the XANES spectrum of water based on a large sample of calculated O-K edges (340 water molecules). This enabled us to decompose the total spectrum into groups with different number of H-bonds in understanding the spectral features.

E. Spectroscopic characterizations, XANES ELNES spectroscopy

(2-3, 6, 9, 12-17, 19, 20, 21*, 27*, 25-28, 30-34, 36-40, 42-44. Total: 31 papers)

Paper [21] is essentially a review article describing the XANES/ELNES calculation using the supercell OLCAO method. This method was developed by us (under many years of DOE support) and has evolved into one of the most effective and versatile methods for spectroscopic properties calculation. The paper pointed out special advantages of this method with examples of applications to a variety of different materials.

Paper [27] describes a novel technique for spectral imaging (SI) of atomic scale microstructures which can extract fine spectral information inaccessible to present day electron microscopy but important for the accurate characterization of nano-materials. This paper addresses this important issue and provides a critical step in the development of new SI method for coupling the dynamical effects and the fine structure variation. The technique is very versatile and can be applied in a variety of ways to enhance the complementary nature of theoretical and experimental work on electron microscopy. This SI technique is demonstrated by applying it to a passive defect model in Si and the same model with doped B. This is a system where current experimental probes have difficulties because of intrinsic limitations. Theoretical calculations can provide crucial and valuable assistance.

F. Large-scale simulations

(1, 5, 10, 22, 24, 34, 35, 36, 39-41*, 44*. Total: 12 papers)

Most of the research work under this DOE grant use large scale computations at the DOE managed supercomputing center (NERSC). We cite two recent examples.

Paper [41] describes the mechanism of structural deformation in a model of DNA double helix by overstretching the double strand step by step. This work proposes an intermediate DNA structure named O-DNA (open-DNA) based on accurate *ab initio* calculations of a 10 Adenine (A) and Thymine (T) base-pairs periodic DNA strand. It clarifies a critically missing part in present theoretical models of the overstretching properties of DNA. There have been long-existing unsettled arguments about the mechanism of DNA overstretching observed in single-molecular experiments. Our study reveals how the atomic and electronic structure variations impact upon each other during the overstretching process, and explains in details how the bonding properties (hydrogen bonds between nucleobases and covalent bonds in the backbone) are affected by the positional adjustments of different functional groups. To Such detailed atomic scale simulations is unprecedented.

Paper [44] reports the mechanical properties and electronic structure of mullite phases using first-principles modeling. The aluminosilicate series ($\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$, $x = 0$ to 1), is an important class of structural ceramics with many applications. No detailed theoretical calculations on its physical properties exist because of the problem with partial occupations in mullite structures. We have constructed large stoichiometric supercell models for the four well-known mullite phases $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, $4\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, and $9\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, plus the two end member in the series, sillimanite ($x=0$) and Al_2O_3 ($x = 1$). The supercell models were fully relaxed using VASP and their physical properties studied in detail and their variations with x (or the alumina content) were properly assessed. The properties calculated include elastic coefficients, mechanical properties (bulk modulus, shear modulus, Young's modulus and Poisson's ratio), sound velocities, electronic structure, bonding, and optical properties. These first-principles results provide the basis for an explanation of the structure and properties of mullite phases at the fundamental level.

List of papers published with acknowledgments to this DOE grant (2006- present). * indicates the work was highlighted above.

Book to be published:

Wai-Yim Ching and Paul Rulis, "*Electronic Structure methods for Complex Materials: The Orthogonalized Linear Combination of Atomic Orbitals*", Oxford University Press, Oxford (2012).

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