THEORETICAL STUDIES ON THE ELECTRONIC STRUCTURE
AND PROPERTIES OF COMPLEX CERAMIC CRYSTALS AND GLASSES

Annual Progress Report
for Period July 1, 1991 - June 30, 1992

Wai-Yim Ching
University of Missouri-Kansas City
Kansas City, Missouri 64110

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Summary

This progress report summarizes the accomplishment of the DOE-supported research program at the University of Missouri-Kansas City for the period 7/1/91 - 6/30/92. This is the second year of a three-year renewal. The major accomplishments for the year are: (a) Initiation of fundamental studies on the electronic properties of C_{60} and related crystals. (b) Study of electronic structures and optical properties of several important ceramic crystals, especially on AlN, SiO_2 and Al_2O_3 . (c) First-principles calculation of total energies and structural phase transitions in oxides, nitrides, and borides. (d) Theory of magnetism in $Nd_2Fe_{14}B$ permanent magnetic alloy.

The major focus for the next year's effort will be on the following areas: (1) Continuation of the fundamental studies on the buckminsterfullerene system with particular emphasis on the alkali-doped superconducting fullerides. (2) Fundamental studies on the structure and properties of Boron and B-related compounds. (3) Basic studies on the structural and electronic properties of metallic glasses with particular emphasis on the magnetic glasses. (4) Further development of the first-principles OLCAO method for applications to super-complex systems.

TABLE OF CONTENTS

Cover Page	1
Summary	2
Table of Contents	3
I. Progress Report	4
HI. List of Papers Published or Submitted	7
III. Efforts of scientific personnel involved	9

I. Progress Report (7-1-91 to 6-30-92)

This section summarizes our major accomplishments for the period from July 1, 1991 to June 30, 1992, thus also includes some of the work currently in progress. They are loosely divided into four categories not necessarily in the order of importance. More detailed description can be found from a large number of published papers which are listed in Section II. The work on the buckminsterfullerene system (C_{60}) is a new initiative in response to the major scientific discovery last year. Other accomplishments follow rather closely to the proposed research projects described in the last year's continuation proposal.

(a) Initiation of the fundamental studies on the electronic properties of C_{60} and related crystals.

In 1991, C_{60} became the molecule of the year. This unique soccer ball-shaped molecule can form crystals and be prepared in thin films. When doped with alkali-metal elements, it becomes superconducting with a T_c as high as 33K, much higher than other members of the organic superconductors. When doped with organic reagents, ferromagnetism is observed. This new class of material is the center of intense research world-wide. Our group has responded to it by performing detailed first-principles calculations on the electronic structure and optical properties of the f.c.c. C_{60} crystal as well as the alkali-doped C_{60} crystals. Our work is state-of-the art and some of them have already been appeared in top journals. We will continue to intensify our research effort in this area in the remaining period of this year and

also the next year.

- (b) Continuation of the study of the electronic structures and optical properties of several important ceramic crystals, especially on AlN, SiO₂ and β -Al₂O₃.

Our major focus on the DOE-supported research has always been in the ceramic materials. We have concluded our investigations on the electronic structures and optical properties of some of the most important ceramic materials such as different polymorphic forms of SiO₂ (α -quartz, β -quartz, β -tridymite, α -cristobalite, β -cristobalite, keatite, cosite and stishovite), β -Al₂O₃, AlN and β -Si₃N₄, MgO and the spinel Al₂MgO₄ etc. Some of the results have already been published while others are waiting to be completed. Very good agreements with the measured data have been obtained for almost all of the crystals studied. Our group has established a reputation for high precision electronic structure calculation of complex ceramics.

- (c) First-principles calculation of total energies and structural phase transitions in oxides, nitrides, and borides.

We have obtained some very good results in the local density total energy calculations and structural phase transitions in BN and elemental B crystals. Progress on SiO₂ crystals and β -Si₃N₄ have been slow mainly because of the complexity of the structures under study demands a much higher accuracy in the total energy calculation. Nevertheless, substantial progress has been made and we anticipate most

of the calculation will be completed by the end of next year.

(d) Theory of magnetism in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnetic alloy.

Our research on the $\text{Nd}_2\text{Fe}_{14}\text{B}$, a high performance permanent magnet with increasing technological applications, has been supported by DOE since its discovery about seven years ago. Our group was the first one to provide the realistic band structure for this material. Since then, we have made steady progress on the study of crystal field parameters and the anisotropic energy in $\text{Nd}_2\text{Fe}_{14}\text{B}$. We have now devised a free-energy approach to study the fundamental mechanism of the magnetization process in this class of materials. The magnetic free energy as a function of magnetization direction is calculated based on a realistic Hamiltonian whose parameters are constructed in a first-principles manner. Results obtained so far indicate this approach is very successful, and can be used to study the magnetization process in other systems as well.

II. List of scientific papers published, accepted and submitted.
(since last report and for the period 7/1/1991 - 6/30/1992)

(A) Work fully or partially supported by the project

- (1) X.L. Yang, S.-H. Guo, F.T. Chan, K.W. Wong and W.Y. Ching, "Analytic Solution of Two-dimensional Hydrogen Atom. I. Non-relativistic Solution", Phys. Rev. A, **43**, 1186 (1991).
- (2) F.T. Chan, S.-H. Guo, X.L. Yang, K.W. Wong and W.Y. Ching, "Analytic Solution of Two-dimensional Hydrogen Atom. II. Relativistic Solution with Chern-Simon Action", Phys. Rev. A, **43**, 1197 (1991).
- (3) Y.-N. Xu and W.Y. Ching, "Selfconsistent Band Structures, Charge Distributions and Optical Properties of MgO, α -Al₂O₃ and MgAl₂O₄", Phys. Rev. **B43**, 4463, (1991).
- (4) W.Y. Ching, G.-L. Zhao, Y.-N. Xu and K.W. Wong, "Orbital-resolved Partial Density of States in YBa₂Cu₃O₇", Phys. Rev. **B43**, 6159 (1991).
- (5) Y.-N. Xu, Yi He and W.Y. Ching, "Distribution of Iron Moments in a-Fe and a-Fe_{1-x}B_x Glasses by First Principles Spin-Polarized Calculations", J. Appl. Phys., **69**(8), 5460 (1991).
- (6) W.Y. Ching, Y.-N. Xu, Y.C. Jean and K.W. Wong, "Application of Band Theoretical Results to Ceramic Superconductors", Superconductivity II, Proceedings of the Symposium on Ceramic Superconductors, the second International Ceramic Science and Technology Congress. Amer. Ceram. Society, Westerville, Ohio. Edited by K.M. Nair, p301, 1991.
- (7) Y.-N. Xu and W.Y. Ching, "Calculation of Ground State and Optical Properties of Boron Nitride in Cubic, Hexagonal and Wurtzite Structures", Physical Rev. B. **44**, 7787, (1991).
- (8) W.Y. Ching, M.-Z. Huang, Y.-N. Xu, W.G. Harter and F.T. Chan, "First Principles Calculation of Optical Properties of C₆₀ in the f.c.c. Lattice", Phys. Rev. Lett., **67**, 2045 (1991).
- (9) W.Y. Ching and Y.-N. Xu, "Electronic Structure and Fe Moment Distribution in a-Fe_{1-x}B_x Glass by First-Principles Calculations", J. Appl. Phys. **70**(10), 6305 (1991).
- (10) Xue-Fu Zhong, W.Y. Ching and Wuyan Lai, "Calculation of Spin-reorientation Temperature in Nd₂Fe₁₄B", J. Appl. Phys. **70**(10), 6146 (1991).
- (11) Y.-N. Xu and W.Y. Ching, "Selfconsistent Band Structures and Optical Properties of All Polymorphic Forms of Silicon Dioxide", Phys. Rev. **B44**, 11048, (1991).
- (12) Y.-N. Xu, M.-Z. Huang and W.Y. Ching, "Optical Properties of Superconducting K₃C₆₀ and Insulating K₆C₆₀", Phys. Rev. **B44**, (Rapid

Communication), **44**, 13171 (1991).

- (13) M.-Z. Huang, Y.-N. Xu and W.Y. Ching, "Band Structures, Density of States and Fermi Surfaces of $C_{60}K_x$, $x = 1, 2, 3, 6$. J. Chem. Phys., **96**(2), 1648 (1992).
- (14) F. Gan, M.-Z. Huang, Y.-N. Xu, W.Y. Ching and J.G. Harrison "Optical Properties of CaF_2 ", Phys. Rev. B. (accepted).
- (15) Dong Li, Y.-N. Xu and W.Y. Ching, "Electronic Structures, Total Energies and Optical Properties of α -rhombohedral B_{12} and α -tetragonal B_{50} Crystals", Phys. Rev. **B45**, March 15 (1992).
- (16). Y.-N. Xu, M.-Z. Huang and W.Y. Ching, "Comparative Study of the Electronic Structures of K_3C_{60} , RbK_2C_{60} , $Rb_2K_1C_{60}$, Rb_3C_{60} and Cs_3C_{60} ", Submitted to Phys. Rev. B (rapid Communication).
- (17) Y.-N. Xu, M.-Z. Huang and W.Y. Ching, "Theoretical Determination of the Pressure Dependence of the Electronic and Optical Properties of f.c.c. C_{60} ". Submitted Phys. Rev. B (rapid Communication).
- (18) Xue-Fu Zhong, and W.Y. Ching "On the Mechanism of First Order Magnetic Phase Transition in $Nd_2Fe_{14}B$ Type Compounds", subm. to Phys. Rev. Lett.
- (19) M.-Z. Huang, Y.-N. Xu and W.Y. Ching, "Pressure Dependence of the Electronic Structure of the superconducting K_3C_{60} ", Submitted to Phys. Rev. B.

(B) Scientific Work not directly related to the grant but representing scholarly work in the general area of condensed matter theory.
(Supercomputer time allocated by Office of Basic Energy Research may have been used in some cases)

- (1) Y.C. Jean, C.S.Sundar, A.Bharathi, W.Y.Ching, P.H.Hor, Y.Y.Xue, R.C. Meng, Z.J. Huang, and C.W. Chu, "Electronic Properties of High Temperature Superconductors Probed by the Positron Annihilation Spectroscopy", Proceedings of 6th International School of Condensed Matter Physics, September 19-29, 1990, Varna, Bulgaria, Edited by J. Marchalle, World Scientific, Singapore.
- (2) C.S. Sundar, A. Bharathi, W.Y. Ching, Y.C. Jean, P.H. Hor R. L. Meng, Z.J. Huang and C.W. Chu, "Positron Annihilation Studies on the Bi-Sr-Ca-Cu-O Superconductor", Phys. Rev B. **43**, 13019, (1991).
- (3) D.L. Huber and W.Y. Ching, "Effect of Disorder on the Trapping of Frenkel Excitons in Three dimensional Systems", J. Statistical Physics, (in press) (1991).
- (4) D.L. Huber and W.Y. Ching, "Oscillatory Decay of Exciton Fluorescence Following Pulsed Excitation of a Disordered Binary Crystal", Accepted by J. of Luminescence

III. Efforts of scientific personnel involved.

(1)	W.Y. Ching, Principal Investigator	
	15% academic year	not paid by the grant
	2 summer months	paid by the grant
(2)	Yong-Nian Xu, Research Associate	paid by the grant
	Xue-Fu Zhong, Visiting Scientist	paid by the grant
(3)	Graduate Research Assistants:	
	F. Gan ^{&}	Paid by the Grant
(M.S. received December, 1991)
	Dung Li	Paid by the grant
(Ph.D. in progress)
	Hong Jiang [#]	Partially paid by grant
(M.S. expected August, 1992)

& Mr. Gan finished his MS degree in December, 1991. He will stay on for 6 months to assist on some on-going research projects.

Newly appointed graduate research assistant.

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