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Review

A theory of the relativistic fermionic spinrevorbital

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The Little Rules and Effect describe the cause of phenomena of physical and chemical transformations on the basis of spin antisymmetry and the consequent magnetism of the most fundamental elements of leptons and quarks and in particular electrons, protons and neutrons causing orbital motions and mutual revolutionary motions (spinrevorbital) to determine the structure and the dynamics of nucleons, nuclei, atoms, molecules, bulk structures and even stellar structures. By considering the Little Effect in multi-body, confined, pressured, dense, temperate, and physicochemically open systems, new mechanisms and processes will be discovered and explanations are given to the stability of multi-fermionic systems for continuum of unstable perturbatory states with settling to stable discontinuum states (in accord to the quantum approximation) to avoid chaos in ways that have not been known or understood. On the basis of the Little Effect, the higher order terms of the Hamiltonian provide Einstein's missing link between quantum mechanics and relativity for a continuum of unstable states. Such continuum of unstable, hidden states determines fractional charges and fractured dipoles (orbitals) that strongly couple with limitations of larger space and shorter times for coupling quantum magnetism (spinrevorbitals) to macromagnetism and gravity (via phasal and group dispersions, respectively) and vice versa and for coupling orbital electricity (spintransorbitals) to macroelectricity and classical (and heat) mechanics (via phasal and group dispersions, respectively) and vice versa.

Key words: Electrons, protons, neutrons, radical catalysts.

INTRODUCTION

The Little Effect and Rules by R.B. Little determine that the spin states of radical reactants, radical catalysts, electrons, protons and neutrons allow and induce revorbital rehybridizations, accelerations and asymmetric dynamics for important transformations to determine symmetric, asymmetric and/or antisymmetric reaction trajectories to specific products. The Little Effect (2000) involves: (1) external magnetic field correlating multiple fermionic spin-revolution-orbitals (spinrevorbitals) of many reacting species; (2) many spinrevorbitals of spectators and/or catalyst species coupling to

physicochemically reacting spinrevorbitals of multiple species; and/or (3) intrinsic multiple, reacting species internally coupling their spinrevorbitals of fermions, producing causes that create effects of changes in physicochemical dynamics and kinetics along physicochemical reaction trajectories for each of these three physicochemically reacting scenarios! Spinrevorbitals are spin and orbital motions of discontinuum states with added new relativistic revolutionary motions of continuum states (quantum forbidden state) as well as relativistic revolutionary motions

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within prior discontinuum states (orbital and spin motions).

The Laws of Ferrochemistry (of resulting physicochemistry of the Little Effect) are listed here. First Law of Ferrochemistry involves the Woodward-Hoffmann Rule (1965) (Woodward, 1942; Hoffmann and Woodward, 1972) and considers that in the absence of or under too weak of a magnetic field, physicochemical reactions progress such that the reactants preserve the total orbital angular momentum in forming products. Second Law of Ferrochemistry involves the Little Rule 1 (2000) and involves that the coupling relationships between systems of physicochemical reactions and itself internally and/or the minimum needed external magnetic field and/or external spin-revolution-orbital (spinrevorbital) matter, energy, momentum, density, and/or acceleration to alter dynamics and kinetics of the system of physicochemical reactions are such that the greater the energy of the physicochemical reactions in space-time then the easier and inherent the internal couplings of spinrevorbitals of the multiple reactants and/or the smaller the minimum needed external magnetic field and/or spinrevorbitals' energy and momentum density in surrounding space time to couple with the physicochemical reactions and alter the course (dynamics) and rates (kinetics) of the physicochemical reactions. The Third Law of Ferrochemistry involves Little Rule 2 (2000) and considers that for systems of small particle densities and high internal magnetic fields in the presence (internally or externally) of sufficient strong magnetic field and/or sufficiently large spin-revolutionary-orbital (spinrevorbital) energy, matter, momenta, density, acceleration and momenta beyond the coupling strength by Law 2 then the physicochemical reaction dynamics is either altered such that the spinrevorbital momenta of the products are larger than spinrevorbital momenta of the reactants in the slow rotational limit of the activating conditions or the physicochemical reaction dynamics is altered such that the spinrevorbital momenta of the products are smaller than the spinrevorbital momenta of the reactants in the fast rotational limit of the activating conditions. Fourth Law of Ferrochemistry involves Little Rule 3 (2000) and considers that for systems of large particle densities and low internal magnetic fields in the presence (internally or externally) of sufficiently strong magnetic field and/or sufficiently large spin-revolution-orbital (spinrevorbital) energy, matter, momenta, density, acceleration and momenta beyond the coupling strength by Law 2 then the physicochemical reaction dynamics is either altered such that the spinrevorbital momenta of the products are smaller than the spinrevorbital momenta of the reactants in the slow rotational limit of the activating conditions or the physicochemical reaction dynamics is altered such that the spinrevorbital momenta of the products are larger than the spinrevorbital momenta of the reactants in the fast rotational limit of the activating conditions.

Rule 2 applies to parts of larger systems, higher energies and orbitals in smaller systems. Rule 3 applies to whole structures, lower energies and orbits. Rule 2 can apply to interior and core of orbitals. Rule 2 and 3 can vary over space and time and over matter, fields, energies, momenta and accelerations. Submicroscopic continuum behave by Rule 3 under transient unstably and hidden tendencies. Macroscopic discontinuum behave by Rule 2 under transient, unstably and hidden tendencies. If apply high fields and or temperatures then macro continuum by Rule 3 can transform to behavior described by Rule 2. On short time scales transient, submicroscopic systems can behave by Rule 3. On transient short time scales, the macroscopic systems can behave by Rule 2. In general over smaller space Rule 2 applies. And over larger space Rule 3 applies. On macroscale systems behave by Rule 3 and over shorter time atomic systems behave by Rule 3 and on macroscales, systems behave by Rule 3 as restricted by $v < c$ and self-interactions. Systems of many atoms behave by Rule 3 for longer times and by Rule 2 for shorter times. Systems of fewer atoms tend to behave by Rule 2 over long time and they behave by Rule 3 over shorter times. Systems of large energy tend to behave by Rule 2 over longer times and they behave by Rule 3 over shorter times. Systems of smaller energy tend to behave by Rule 3 for longer times and they tend to behave by Rule 2 over shorter times. Rule 2 and Rule 3 are applied to initial and final states of systems and then the Rule for the activated transition state is assessed for various processes.

Such aspects of the Little Effect and Rules can cause spin frustration of the orbital symmetry of Woodward-Hoffmann reaction dynamics (Woodward, 1942; Hoffman and Woodward, 1972). The implications of the Little Effect and Rules will lead to novel chemical reaction dynamics of solute in paramagnetic and ferromagnetic media and the useful control of these transformations by external magnetization. Such novel chemical reaction environments will contribute conditions such that radical intermediates can be controlled by external magnetic field so as to select between Lewis σ bonds, Lewis π bonds and various bond rearrangements. G.N. Lewis first determined electron sharing as the basis of covalent bonds within molecules and he first suggested that radicals might be studied by using external magnetic field (Lewis and Calvin, 1945). M. Kasha developed theories for energizing molecules and molecular energetic redistribution within molecules {Kasha Rule} (Kasha, 1963). M. A. El-Sayed determined that optical absorption between certain orbitals may induce intersystem crossing due to the intrinsic orbital interactions between the excited electron and its ground state electron partner for one $e^- \cdots e^-$ pair dynamics {El-Sayed Rule} (ElSayed, 1963). The Little Effect determines spin induced revorbital asymmetric mechanics that can result from radical (fermionic) interactions in densely reacting media of many $e^- \cdots e^-$ pairs and many quanta and high energy

density. Whereas the El-Sayed Effect considers Lorentzian Effects between two electrons going into different orbitals for promoting intrinsic intersystem crossing, the Little Effect involves phenomena whereby the Lorentzian Effects by dense spin (orbital, rotational, energetic, momental and/or accelerative) environments (more than two) cause altered electronic reorbital motions. Moreover on the basis of the Little Effect, an external magnetic field may orchestrate desired reaction trajectories. On the basis of the Little Effect, not only can radicals be analyzed by external magnetic field according to G.N. Lewis but their reactions may also be controlled by external magnetic field.

In general in addition to chemistry, such spin, reorbital and magnetic phenomena associated with these fermions provide a basis for understanding physical transformations. It has been stated that magnetism organizes the universe (Vlemmings et al., 2002). Beyond dynamics, the Little Effect and Rules demonstrate such magnetic ordering even on the minute scales of molecules, atoms, nuclei and nucleons. For instance, spin is intrinsic to the existence of fermions: n , e^- , p^+ (Fermi 1926; Lewis, 1936; Pauli, 1932; Fermi, 1930; Dirac, 1979). Spin is an aspect of the most fundamental particles: quarks and leptons. On the basis of the Casimir Effect (Lamoreaux, 1997; Casimir, 1948) and the Meissner Effect (Meissner and Scheffer, 1930; Meissner et al., 1934), the spin is thought to contribute to the stability of such point particles against their self-internal repulsions and self-disintegrations. The Little Effect explains the Meissner Effect. The spin and resulting magnetic field of the charge in motion generates a magnetic field that holds the charge together, thereby organizing the internal structure of the universe on the scale of point particles by Rules 2 and 3. The same spin motion that holds the electron together (by Rule 2) causes its disintegration for its displacement under an external force (by Rule 3) and its revolution about protons (and even its own trajectory) and affects its fusion to the proton to form a neutron (by Rules 2 and 3). On the basis of the Little Effect, fermionic spins on the grander scales accounts for the statistics and organization of nucleons, nuclei, atoms, molecules and bulk materials and even stellar and galactic material assembles on the basis of Rules 1-4. As a result of spin and the resulting magnetism causing order, the syntheses of materials on these various scales must take spin and rotational effects into consideration. Moreover spin and reorbital motions contribute to symmetric aspects for various transformations such as beta, reverse beta, fusion, fission and chemical dynamics. For example, asymmetric spin induction of asymmetric reorbital dynamics (the Little Effect) has provided the foundation for a comprehensive mechanism of carbon nanotube formation (Little, 2003) and also the resolution of the diamond problem (Little et al., 2005). Novel properties of CNT such as H storage and its electrochemistry (Musameth,

and Wang, 2005) may be explained by spin phenomena and reorbital motions according to the Little Effect. The puzzle of reducing the atmosphere (nitrogen) by the Haber process ($N_2 + H_2 \rightarrow NH_3$) (Haber, 1922) is better understood and advanced based on spin induced reorbital effects of rehybridization as outlined by the Little Effect. The Little Rules also apply to important reaction effects associated with singlet oxygen with explanations for its distinct reactivity relative to triplet oxygen. Singlet oxygen has distinct reactivity relative to triplet oxygen (Braun and Oliveros, 1990; Kearns, 1969) due to the different spin induced rehybridizations in its reacting partner for accessing different structural products.

HAMILTONIAN

The Little Effect and Rules include higher order terms of the Hamiltonian that contribute significant kinetic factors to reaction dynamics for discriminating various product bond symmetries and statistics. Obviously, for some thermodynamic systems the higher order spin, reorbital and magnetic interactions of the Hamiltonian cannot contribute to thermodynamic stable state as does the Columbic (electric) factors (also possibly dominating Newtonian gravitational interactions, weak interactions and strong interactions in some systems), but in many systems the spin effects and reorbital motions may discriminate and select between various metastable states and even dictate the transformations (Lebedev et al., 1992; Fermi, 1936) on the basis of Rules 1-4. F.A. Cotton has demonstrated some of these spin and magnetic effects in some 3d metal compounds (Clerac et al., 2001). Also in some dense systems (with large charge, with large kinetic energy and with high spin densities and consequent rapidly organizing motions), the magnetic, spin and reorbital interactions can be tremendous with significant and possibly dominating influences on the Hamiltonian by the Little Effect. But even with thermodynamic instability, the transient formations of reorbital varieties by spin inductions may cause important ultrafast catalytic effects within such systems (Little, 2003; Little et al., 2005) by the Little Effect. On the basis here of the Little Effect, such ultrafast catalytic effects are a future area for femto-chemical analysis by current femtolaser spectroscopy (Zewail, 2001). Such higher order terms can contribute to antisymmetric, asymmetric and non-preservation of orbital dynamics during chemical reactions in paramagnetic and/or ferromagnetic environments so as to compliment the Woodward Hoffmann Rule (Woodward 1942, Hoffmann and Woodward, 1972) of orbital preservation during chemical reaction dynamics. These kinetic effects on chemical reactions according to the Little Rules are most obviously discerned in chemical systems involving atoms associated with the Russell

Saunders coupling scheme, rather than the jj coupling scheme.

With more terms of the Hamiltonian, Einstein's missing part (Einstein et al., 1935) is determined as the complex revolutionary and correlational (spinrevorbital) motions of dense, confined spins and charges in rapid motions for a continuum of unstable states with nonclassical quantum states determined by the stationary states by Rules 1 and 2 relative to perturbative induced unstable continuum states by Rules 1 and 3 by spinrevorbic, complex fermionic motions. On the basis of the Little Effect, here it is suggested that the important crucial revolutionary $e^- \rightarrow e^-$ (spinrevorbital) motions (determining the fermionic correlation) are missing in the Hamiltonians of subatomic particles, atoms and other {with Lorentz (L) frame} systems of densely confined, temperate matter, energy, and motions. These missing fermionic, revolutionary (spinrevorbital) motions and interactions contribute to ultrafine structures of such systems such that the finer structures determine more of a continuum by Rule 3. This continuum in L frame caused by the missing revolutionary (spinrevorbital) motions results from and involves states of unstable perturbation in L frame (by Rules 1, 2 and 3) that readily and efficiently transform to stable quantum mechanical, discontinuum (by Rules 1, 2, and 3) states for explanation and determination of such mysteries as gravity, tunneling effects (Hush and Ulstrup, 1997), Raman Effects (Kastha, 1976), fractional quantum Hall Effect (Schwarzschild, 1998), superconductivity (Meissner, 1932), ferrimagnetism (Neel, 1971), solar neutrino problem (Rajasekar, 2005), neutrino oscillations (Ceolin, 2003), Josephson Effect (Pippard, 1977), tautomerism, pyconuclear (Cameron, 1959) processes and other oddities not fully captured by Schrodinger's and Dirac's equations. Without these higher order missing parts, the discontinuity of states manifest; this discontinuity is actually the stable states that exist between perpetual, ever-present, reversible perturbations to this ultrafine continuum of unstable states; such perturbations can explain gravity, macromagnetism, macroelectric, Newtonian mechanics, thermodynamics, and inertia in Poincare (C) frame by Rule 3. Such continuum states (that exist inter and between discontinuum states) also provide submicroscopic origins and explanations of gravity, inertia and heat for Einstein's missing variables. Furthermore within the discontinuum (orbitals), there exists intracontinuum states of simultaneity and superpositions which can be reasoned by Rules 1 and 2 and a blend of Rules 2 and 3 relativistically within a given orbital and less so between many orbital (discontinuums). Such blend of Rules 2 and 3 give relativistic explanation of wave particle duality as by Rule 3 the particle tends to delocalize and by Rule 2 the wave tends to localize.

Such continuum, unstable states of perturbations in L frame is the basis for Planck blackbody and quantization phenomena (Planck, 1920) by Rules 1-3.

The oscillations of the blackbody can execute a continuum (hence its blackness) of oscillations by Rule 3. But on the basis of the quanta certain vibrational energy distributions are more probable and thereby more statistically stable by Rule 3. Quantum mechanics was born by Planck on the basis of this seeming energetic discontinuity in L frame. In essence, there is a continuum of oscillations but the discontinuum is actually an approximation reflecting the statistical stability (higher probability) of these quanta of oscillations (for relativistic phasal dispersions of spintransorbitals) and also reflecting the infinity of states between quanta such that conservation of energy would not allow the statistical oscillation of all such continuums (between quanta) of oscillations. So the continuum exists, but the oscillators just distribute the energy among specific modes (for a discontinuum) (by Rules 2 and 3) on the basis of the temperature. On this basis, the quanta do not reflect the possible mechanics but the more probable mechanics and dynamics (and hence the probabilistic nature of quantum mechanics and Born's subsequent interpretation). Here it is interesting to note this dependence of the quanta on the total energy and how the distribution changes with temperature. As the energy of the system increases the possible energetic states approach more of a continuum (by Rule 3). Thereby here it is wondered if in the limit of infinite energy if all or more of the continuum is manifested. The oscillations of the atoms depend directly on the oscillations of electrons. Thereby a continuum of atomic oscillations would determine a continuum of electron (or other fermionic systems) motions on the basis of a Rutherford type atom (Rutherford, 1914) and a discontinuum would determine electron motions on the basis of a Bohr type atom (Bohr, 1914) with Schrodinger (Schrodinger, 1926) and Heisenberg (Heisenberg, 1926) implications to the structure of the atom. The atomic oscillations are vibrational (spintransorbitals) at lower temperatures and revolutionary (spinrevorbitals) at higher temperatures. At a given temperature and energy, the electrons of lighter mass can exist in spinrevorbitals and lighter mass particles can also exist in spinrevorbitals as they can undergo transitions from spintransorbitals to spinrevorbitals at lower temperatures. At higher temperatures and energies, more massive nuclei can undergo phase transitions from spintransorbitals to spinrevorbitals as they may exist in stellar environments for superfluidity in stellar environments by such phase changes of nuclei to spinrevorbitals from spintransorbitals. Such transformations of particles from spintransorbitals to spinrevorbitals with increasing kinetic energy and temperature occur due to the inability of the fermionic motion to have $v < c$ in accelerating at the extremities of vibrations and by consequent magnetic self-interactions as they approach the speed of light at the extremes of spintransorbitals and the resulting magnetic self-interactions transform vibrations to rotations.

In the resulting spinrevorbital motions and the high internal magnetism of self-interactions, the fermions no longer have extremes of linear motions requiring ultrarelativistic speeds to vibrate as the circular or elliptic motions mix directions of space and time by general theory of relativity for greater stability of the spinrevorbital relative to the spintransorbital at such higher energies.

Here with such spintransorbital to spinrevorbital motions, there are discontinuum (phasal) (self-interacting) and intervening continuum (group) (non-self-interacting) dispersions of the fermions. It is important to note that in the previous paragraph a positive center with surrounding electron lattice (circular and elliptic and spiral trajectories) is discussed but the structure and dynamics may also apply more generally to other systems of negative centers and positive lattices or centers of N magnetic poles with surrounding S magnetic poles (circular and elliptic and spiral trajectories) and vice versa and centers Dark or Bright gravities (hyperbolic and parabolic trajectories) and vice versa and mixed forces and trajectories therein. Here it is suggested that a continuum exists but not as in the Rutherford style atom but the continuum exists with order within the orbit configured by Bohr model; with order within the orbital as configured by Schrodinger and Heisenberg models and their shells, subshells and orbital; and with order within the spin as configured by Pauli (Pauli, 1932), Fermi (Fermi, 1930) and Dirac (Dirac, 1979) models with their electron spin (fermionic); and moreover based on the ultra-hyperfine order by the hyper-configuration by this Little Effect of electron --- electron revolutions (vibrations) superposed on spin and orbital motions for spinrevorbital (spintransorbital) motions (blend of Rules 2 and 3). This complex superposed revolutional (vibrational) motions within orbital motions is coined here revorbital (transorbital) motions, which in combination with spin becomes spinrevorbitals (spintransorbitals) (discontinuum). The here proposed spinrevorbital (spintransorbital) motions (blend of Rules 2 and 3) of fermions cause a continuum of ordered unstable states (Rule 3) with a few stable modes (quanta)(Rules 2) that rapidly develop from relaxation from perpetual disturbances (by gravity, heat and inertia) to these virtual discontinuum stable states (for the quantum mechanical approximation). So here it is demonstrated that quantum mechanics is not wrong, it is a great approximation of some higher but unstable, relativistic order. Within such relativistic order, the transition of continuum spintransorbitals and spinrevorbitals to thermal energy, mechanical energy, macroelectric energy and to gravity and macromagnetism (respectively) and vice versa can be explained and such coupled spintransorbital and spinrevorbital continuum in L frame can organize and synchronize heat, thermal energy, mechanical energy, macroelectric energy, gravitational energy and macromagnetic energy of C frame and vice versa depending on conditions.

Such order in instability (far from equilibrium) has been demonstrated in science (Prigogine, 1978). The extreme, ultra-fine structure of instability develops by the Little Effect on the basis of spin induced revolutional motions based on relativity that is superposed on orbital motions for spinrevorbital motions. Here it is suggested that the continuum and its instability are the results of relativistic effects of the correlated revolutionary nature (spinrevorbital) of the fermionic electrons (fermions). Upon perpetual excitation to these many, many submicroscopic, continuum unstable states (in underlying L frame) (Rule 3) from discontinuum, stable states, the unstable continuum rapidly relaxes back to the stable discontinuum states by Rule 2 (for gravity, inertia and heat mechanisms). Inertia of bulk objects can be explained by such motional induced excitations of many, many submicroscopic unstable continuum states (in underlying L frame) (by Rule 3) as the resulting many, internal, continuum states of the whole object disrupt internal self-interactions, quantizations and discontinuum states (of many L frames composing the whole object); thereby the many continuum submicroscopic states consequently rapidly relativistically in L frames relax back to discontinuum states (by Rule 2) with transfer of momentum to C frame to oppose the perturbing bulk motion of objects for inertia mass in C frame. Gravitational interactions of bulk objects in C frame can also be explained by such gravitational induced excitations of many many submicroscopic, unstable, continuum (spinrevorbital group dispersed) states of the many L frames composing the whole object (by Rule 3) or the resulting many external continuum states of external objects disrupting the many internal self-interactions, quantizations and discontinuum states making up the whole object, thereby the many gravitons of internal continuum states rapidly in L frames of the object relativistically relax back to discontinuum states (by Rule 2) with release of exciting gravitons and an opposing counter force on the object by (Newton's Third Law) to effect gravitational force on the object by other objects where from the gravitons came.

Macromagnetism and magnetic interactions in C frame can also be explained by such magnetic induced excitations of many, many submicroscopic, unstable continuum (spinrevorbital phasal dispersed motions) states (in underlying L frames) within the whole object (by Rule 3) or the resulting many external continuum states disruptions of the many internal self-interactions, quantizations and discontinuum states (in underlying L frames) making up the whole object, thereby the C frame magnetic field of other objects alters the internal L frame continuum states of the object under consideration with consequent relativistic relaxation back to the discontinuum states with release of the exciting C frame magnetic field and opposing counter force on the object (by Newton's Third Law) to effect macromagnetism on the object by other magnetic objects. Macroelectricity

and electric interactions in the C frame can also be explained by such electric induced excitations of many, many submicroscopic unstable continuum (spintransorbic phasal dispersed motions) states (in underlying L frames) within the whole object (by Rule 3) or the resulting many external continuum states disruptions of the many internal self-interactions, quantizations and discontinuum states (in underlying L frames) making up the whole object, thereby the C frame electric field of other objects alters the internal L frame continuum states of the object under consideration with the consequent relativistic relaxation back to the discontinuum states with release of exciting C frame electric field and an opposing counter force on the object (by Newton's Third Law) to effect macroelectricity on the object by other magnetic objects. Heat and thermal effects in the C frame can also be explained by such fractional electric excitations of many, many submicroscopic, unstable (spintransorbic, group dispersed motions) states (in underlying L frames) within the whole object (by Rule 3) or the resulting many external continuum states disruptions of the many internal self-interactions, quantizations and discontinuum states (in underlying L frames) making up the whole object, thereby the C frame thermal energy of other objects alters the internal L frame continuum states of an object with the consequent relativistic relaxation back to the discontinuum states with release of the exciting external C frame thermal energy and the lack of a counter force on the object (by Newton's Third Law) as the group dispersed intermediate spintransorbital transiently did not ordered the heat so the released heat is not able to induce net force (or do work) on the object. Although no net force is induced on the whole objects due to heat absorption and release, it is important to note that in the absorbed state, the heat is transiently organized but such ordered heat is hidden in the transient group dispersed many spintransorbitals (of L frames) of the object.

The instability of the continuum states has to do with statistical improbability of distributing the energy in such states by Rules 1-4. It is on this basis that here the Raman Effect (Kastha, 1976) is explained within a discontinuum of states such that the unstable quanta of the Raman state involve the unstable (statistically unprobable motion and interaction) spinrevorbital motions of electron pairs by Rule 3 such that the spinrevorbital of this instability determines an acceleration that offsets there Coulomb repulsive force and pulls them back into stable stationary spinrevorbital (discontinuum by Rule 2) states of lower energy by photon release. The photon can disrupt the stable quanta to a higher energy unstable continuum state but within this continuum unstable state the revolutionary motion of self-interactions is broken so the electrons rapidly relax back to the lower energy discontinuum stable state by releasing the photon for the Raman Effect by Rules 1-3. The exciting photons accelerate the electrons counter to their mutual internal

accelerations within the stable spinrevorbital (discontinuum) state. If the photon acceleration is less than the spinrevorbital (excited) accelerated motion then the photon causes a virtual (continuum) state of the spinrevorbital and is immediately released so the lower energy stable spinrevorbital reforms. If a photon of sufficient and matching energy is absorbed by the correlated stable (discontinuum) spinrevorbital motion of the electrons of a lower energy state, then the relativistic electron --- electron spinrevorbital motion can be transformed such that the one electron is excited to upper level stable (discontinuum) quanta for different spinrevorbital (discontinuum) motion and mode by Rules 1 and 2. On the basis of the Little Effect, it is important to consider the nature of these spinrevorbital transformations. The unmatching Raman photon excited the electron pair into different revolutionary motions with possibly similar orbital motion (Born-Oppenheimer and Franck-Condon Laws). It is important to note this spinrevorbital theory gives an explanation of how the system transforms from discontinuum to discontinuum across an intervening continuum. The photon absorption by the lower energy discontinuum (of Rule 2) transforms the discontinuum into the intervening continuum (of Rule 3), which is described by Rule 3 where by the multitude of unstable states of the continuum distribute the energy and motion within the continuum and due to the intensity of energy and motion the excess energy is redistributed into upper level discontinuum by Rule 2 rather than release of photon. But at some later time the system may release the photon to relax back to the lower energy discontinuum.

Here it is important to note that the kinetics of spin dynamics exceeds $e^- - e^-$ revolutionary dynamics and the $e^- --- e^-$ revolutionary dynamics exceed the kinetics of orbital dynamics for the superpositioned spinrevorbitals by Rule 1. So spins can flip; revolutions cannot flip (the weak interaction is a manifestation of such revolutionary flip) due to the $v > c$ essence of the revolution and the inability of the relativistic revolutionary's integrity to flip its direction of motion. Large revolutionary flips are related to bright and dark gravitational productions. It is by these dynamical aspects by the Little Effect that spin and revolutions are so important for certain disequilibria and structural changes. But now the Raman photon cannot alter the spin multiplicity but it can alter the $e^- --- e^-$ revolutionary modes for fixed revorbital modes. The statistical improbability of the resulting continuum revolutionary modes leads to the reformation of the discontinuum by photon release for relaxation to the more probable $e^- --- e^-$ revolution of the lower energy stable discontinuum state by Rule 2. However, if the Raman photon has high enough energy, then it can excite large enough $e^- --- e^-$ revolutions such that the revolutions couple to the orbital modes of high (discontinuum) orbital state to transform the lower orbital mode to an outer orbital for different spin revorbitals in an upper level,

stable discontinuum mode by Rule 2.

These explanations by the Little Effect and Rules account for violations of the $\Delta l \neq 1$ for many photo-physical processes. Furthermore the different spinrevorbital motions of the excited, stable states relative to the ground state may allow spin transition (El-Sayed Rule) (El_Sayed, 1963). Here the Little Effect explains the El-Sayed Rule. It is important to note that in addition to the El-Sayed Rule, an external magnetic field can change the Hamiltonian for triplet formations within this upper level discontinuum stable state (and also within upper level, unstable continuum states). By the Lewis Rule, phosphorescence (Lewis, 1945) requires spin change for the electron to relax from the triplet state by photon to the spinrevorbital bosonic ground state (for a blend of Rules 2 and 3). The slow phosphorescence relative to fluorescence may be explained by relativistic limits of blending Rules 2 and 3 between orbital modes and spinrevorbital modes. In such a case, the external magnetic field disrupts the bosonic spinrevorbital for changing the statistics to fermionic states. But stronger magnetic fields are needed to break the bosonic spinrevorbitals of the lower energy virtual states by Rule 1. It is on this basis that the bosonic spinrevorbital motions repel magnetic fields by Rules 2 and 3 explaining the Meissner Effect. The field created within the bosonic spinrevorbital pair by relativistic motion (current) is too strong to be aligned by the weaker external magnetic field so the external field causes an opposing circulation within the bosonic spinrevorbital for repulsion.

It is important to note that the strength of the spinrevorbital motions depend on the bond strengths of the bosons by Rule 1. So the energetic ordering of bosonic spinrevorbital motion is $\sigma > \pi > \delta$ for the order of increasing spiral strength and correlation. Phonons and high temperature can assist the external magnetic field breaking the bosonic spinrevorbital states to transform them to fermionic pairs. It is on this basis that R. B. Little breaks π bonds of graphite at 900°C in hydrogen atmospheres and Fe media with 20 tesla magnetic field for diamond formation in the open atmosphere (by Rules 1-3).

So this account of the Little Effect explains the Meissner Effect (Meissner and Scheffers, 1930; Meissner et al., 1934) as a relativistic stabilization of electron --- electron spinrevorbital motions that will not allow magnetics disruption by weaker external currents relative to the greater internal currents of bosonic spinrevorbital currents by Rules 2 and 3. On the basis of the Little Effect, here it is suggested that the spinrevorbital motions and the consequent relativistic effects and revolutionary statistical effects cause the instability of the continuum virtual states by Rule 3 and the quanta effects for disrupting the lower energy revolutionary motions into higher energetic stable excited revolutionary correlated states of fermionic distribution within shells, subshells, orbitals and multiplicity by Rule 2. The photoelectric effect

and Einstein's photon quanta (Einstein, 1906) are consistent with this view of the Little Effect. The electromagnetic radiation behaves as quanta because only chunks of sufficient energy are able to instantaneously (within the speed of light) disrupt the stable electron -- electron spinrevorbital motions into different states of electron --- electron spinrevorbital motions or eject the electron from the orbital (photoelectric effect) by Rule 3. If the photon chunk has insufficient energy then a continuum of unstable (continuum) states (virtual states) are excited by Rule 3, which (within the speed of light) rapidly relax to the stationary (discontinuum by Rule 2) state due to relativistics and revolutionary statistical factors of the spinrevorbital motion. The beauty of this explanation by the Little Effect is revealed by its consistency with light-matter interactions, as well as laser effects on matter. Unlike incoherent light, laser light is coherent, polarized and in phase (Shimoda, 1979). Such properties of laser light allow multiphotons of coherence and synchronization to simultaneously act on many virtual continuum states of nonmetals in a way not possible by incoherent light such that the laser photons can compete with relativistic motion within the spinrevorbital virtual state of nonmetals so as to excite the unstable intermediary (continuum) virtual state of the spinrevorbital to upper level stable (discontinuum) spinrevorbital states of nonmetals or even cause ionization before the virtual state can revolutionally relax and release its photon (by Rules 1, 2 and 3). Quite interestingly and amazingly, a metal can internally lase incoherent light to affect the same process so long as the incoherent light has short enough wavelength (by Rules 1, 2 and 3). The lattice of metals can internally lase incoherent light by its internal spinrevorbitals. Remarkably RBL considers later such internal lasing within metals to affect the opposite dynamics of electrons collapsing on nuclei rather than electrons ejection by photoelectric effect under differing conditions. But intense incoherent light is not likely to do this with any significant probability within nonmetals because the photons although of the same frequency are very improbable of the same polarization and phase for proper phase relation and timing with the unstable virtual states caused by the first photon for collectively ejecting the electrons.

For consistency, it is important to demonstrate on the basis of the Little Effect, the application of the spinrevorbitals even to the one electron hydrogen atom. One can easily image complex revolutionary orbital motions (spinrevorbitals) of multi electron systems, but even the single electron in the hydrogen atom is better understood on the basis of spinrevorbitals. Niel Bohr provided a great model of the hydrogen atom (Bohr, 1915) on the basis of mixing classical mechanics with certain quantum hypotheses motivated by Planck (Planck, 1920). Bohr's model accounts for Rydberg's curves fitting of optical spectra of the hydrogen atom. But

Bohr's model failed for multi-electron atoms. The hyperfine structure of hydrogen in magnetic field (Bohr, 1914) due to Zeeman Effect and Lamb shift requires a different Hamiltonian than the Bohr model. Here on the basis of the Little Effect, other properties of the hydrogen atom beyond the Zeeman Effect (Onnes, 1921) and the Lamb Shift (Barut and Kraus, 1982) are not accounted for by the Bohr's model, nor by Schrodinger 's model (Schrodinger, 1926) and not even by Dirac's (Dirac, 1979) Hamiltonians. Certain chemical properties of hydrogen (such as hydrogen-bonding, acidity, hydrogen in metals) are not fully captured by Dirac's (Dirac, 1979) relativistics quantum mechanics. A more thorough account by the Little Effect involving relativistics of both electron spin, revolutions, orbital motions and relativistics of electron --- proton correlated motion (spinrevorbitals) give a better perspective of hydrogen's properties.

On the basis of the Little Effect, although the electron orbits the proton in orbitals, the electron also revolves (and vibrates relativistically) in its orbital motions for many simultaneous effects even in the 2 body systems. Here it is suggested that the electron spinrevorbital motions are caused by its self-interactions within its own orbitals for blend of Rules 2 and 3 within the orbitals. The electron spirals in its orbital motions on the basis of its spin-interactions with its own orbital motions so as to stabilize its orbital existence near the nucleus. These self-interactions cause greater complexity of hydrogen beyond Bohr's model and even Dirac's model by higher order complex interactions: e^- spin --- p^+ spin interactions, e^- orbit --- p^+ spin interactions, e^- revolution --- p^+ spin interactions, e^- spin --- e^- orbit interactions, e^- spin --- e^- revolutionary interactions, e^- orbit --- e^- revolutionary interactions. These higher order self-interactions of the electron cause the unstable continuum (by Rule 3) of possible states and the consequent probabilistic behavior. On this basis, the electron's position and motional phenomena are manifested probabilistically in wave pattern described by the wavefunction and Born's interpretation. On this basis, the Zeeman Effect, Lamb shift and unique chemistry of hydrogen are understood as a modification of this Dirac Hamiltonian such that the spin, orbital and revolutionary effects contribute more spinrevorbitals for different continuum wavefunctions and energies. Here on the basis of the Little Effect, it is demonstrated that strong external magnetic fields and spin --- spin exchange environments lead to novel chemical, physical and catalytic properties and systems for hydrogen as in novel CNT and diamond formations, novel lower temperature metal eutectic, unusual electrolysis, protolysis, hydrogen bonding and anomalous pycnonuclear fusion. For example a greater understanding of acidic protons can be reasoned by considering these fine revolutionary motions of e^- --- e^- pair near p^+ so as to magnetically bind the e^- --- e^- pair but Coulombically break the bond in acidic and basic compounds. In general such greater complexity in

hydrogen, increases for even more complexity in multi electron atoms.

These implications of the Little Effect for more complex (continuum) revolutionary electron --- electron motions and correlations provide the ultrafine structures that explain the wavefunction and its probabilistic determination of particle position (Δx) such that different positions of the confined particles would exhibit different revolutionary motions (Δp) on the basis of this ultrafine structure. Here by the Little Effect on the basis of this missing part (spinrevorbital), the Hamiltonian by Rule 3 becomes more subject to relativistic effects due to relative motion of pairs of revolutionary and spinning particles relative to other particles by Rule 2. This consideration more thoroughly links relativity and quantum mechanics with dramatic implications concerning the approximate nature of quantum mechanics and Rule 2 becoming a foundation for Rule 3. Pauli (Pauli, 1932) and Dirac (Dirac, 1979) began this linkage of quantum mechanics and relativity with their experimental and theoretical determination of the electron spin motion. Here by the Little Effect, this integration of relativity and quantum mechanics is furthered by introducing an even finer internal electron-electron revolutionary dynamics, superimposed on electron pair orbitals for spinrevorbitals about nuclei. Here it is suggested that excluding such (missing) revolutionary (continuum) spinrevorbital motions by Rule 2 of the correlating pair causes the uncertainty principle by Rule 2. The exclusion of the missing revolutionary motions (Δp) of correlations and the consequent less known interactions (Δx) limits the knowledge relative to the more detailed (revolutional) Hamiltonian for consequent greater uncertainty. Therefore on the basis of the Little Effect, the spins, fermions, and charges cause revolutionary (continuum) (spinrevorbital) motions for pairings for correlations and higher order terms of the Hamiltonian that determine nonstationary continuum with novel implications concerning the exactness of the discontinuous, probabilistic nature of quantum mechanics.

On the basis of the Little Effect, the inclusion here of novel revolutionary (continuum) spinrevorbital motion in the Hamiltonian is analogous to the inclusion of spin and higher order magnetic interactions by Dirac (Dirac, 1979). By doing this with relativistic inclusion, the spin naturally popped out by Dirac's relativistic (Dirac, 1979) modification of the Schrodinger equation (Schrodinger, 1926), which led to a better description of atomic, molecular and matter-light interactions and accounted for Pauli's exclusion principle (Pauli, 1932). Here of the basis of the Little Effect, an analogous addition (as by Dirac) to the Hamiltonian of these revolutionary (continuum) motions (superposed orbital and spin motions for spinrevorbital motions) results in more accurate (but unstable) detailed continuum of states (but unstable states) that will explain such effects as tunneling, Raman

Effect, superconductivity, low temperature fusion and even inertia, gravity and heat and more. On the basis of such complex revolutionary internal motions of fermions and their absence in the Hamiltonian, the wave nature of the confined fermions arises in terms of the wavelength which corresponds to the length scale (Δx) of the uncertainty in its position which arises due to the missing correlated (continuum) revolutionary bosonic (fermionic) pair motions (Δp). The neglect of the correlated (continuum) revolutionary motions (Δp) causes an approximate location (Δx) for uncertainty. On this basis of the Little Effect and correlated revolutionary motions of fermions, the experimental de Broglie wavelength (de Broglie, 1927) is explained on the basis of the nonlinear motions and revolutionary (spinrevorbital) tensions impressed on electrons, neutrons and/or protons by an atom or many atoms in molecules or by a diffracting crystal lattices as observed by Davisson and Germer (Davisson and Germer, 1928). It is quite remarkable that the experiment of Davisson and Germer (Davisson and Germer, 1928) employed a Ni crystal with its ferromagnetism, which made it easier to discern what appeared in the quantum approximation to be electron waves but here it is determined as higher order scattering of the incident fermions by the fermionic lattice spinrevorbitals. The wavelength of diffracted fermions is more a complexity of ultrafine temporal and spatial dependent lattice states that nonlinearly accelerate the fermions. The uncertainty involves the complexity of such ultrafine effects and the extreme difficulty with measuring and observing the dynamics as the continuum by Rule 3 is hidden.

NUCLEON CONFIGURATION

The nucleus consists of protons and neutrons. Protons and neutrons are fermions with spin of $\frac{1}{2}$. The proton consists of quarks. The neutron also consists of quarks. The quarks are subject to the strong force. The strong force holds the nucleons together and residually holds the nucleus together. The strong force is on the order of a hundred times greater than the electric (Coulomb) force. Quarks possess both charge and spin. The electron has charge of -1 . The up-quark has charge of $2/3$. The down-quark has charge of $-1/3$. The electron has mass of $0.000511 \text{ GeV}/c^2$. The up-quark has mass of $0.003 \text{ GeV}/c^2$. The down-quark has mass of $0.006 \text{ GeV}/c^2$. The proton consists of two up-quarks and one down-quark for a net charge of $2/3 + 2/3 - 1/3 = +1$. The neutron consists of two-down and one up-quark for a net charge of $-1/3 - 1/3 + 2/3 = 0$. The leptons and quarks have the property of spin. They have spin such that they are fermions. Fermions have spin of $\frac{1}{2}$. Bosons have spin of 1.

What is spin? It denotes symmetry according to rotation. Zero spin behaves like a point. Spin of 1 has

symmetry of rotation 360° for indistinguishability. Spin $\frac{1}{2}$ has symmetry of rotation 720 degrees for indistinguishability. Spin of two is indistinguishable after rotate of 180 degrees. Leptons have spin of $\frac{1}{2}$. Quarks also have spin of $\frac{1}{2}$. The electrons and quarks must be rotated 720° (rotate twice) for indistinguishability. The spin is an aspect of subatomic particles and their possible constituents. Because of the charge of these particles and their internal motion, the spin attributes magnetic properties to these fundamental entities (Fermi, 1926; Pauli, 1932; Fermi, 1930; Dirac, 1979). Such spin magnetism is an essential aspect of the statistics, the order, the structure and (as here reported) the dynamics of these fundamental particles even in their assembly into complex structures of nucleons, nuclei, atoms, molecules, bulk matter, planets, stellar, galactic and larger systems thereof.

Measurements at CERN have demonstrated that the proton spin is not simply a result of summation of its quark spins (Nassalski, 1997). This research has demonstrated that the proton and its spin are a lot more complicated. Here it is suggested that the quarks move relative to each other. On the basis of the Little Effect, here it is suggested that the two up-quarks of the proton revolve (correlate) relative to each other to minimize their electric repulsion. This revolution of the up-quarks in their relative spins and magnetisms causes a magnetic attraction that opposes the electric repulsion of the two up-quarks of the proton. According to the Little Effect, this effect of the revolution (correlation) (spinrevorbital) on the pairing of the up-quarks is a spin induced revorbital motion that compensates the Coulombic repulsion of the two up-quarks of the proton. The two revolving up-quarks also revolve about the down-quark in the proton. Here it is suggested that the quarks are bound relativistically together on the basis of these relative revolving, accelerating motions (correlations) in their spin-magnetic and Coulombic fields. On the basis of the Little Effect, the strong force is explained as relativistic revolutions (spinrevorbital) (correlation) of the quarks for relativistic blend of Rules 2 and 3 as the quark motions and energies blend from one moving among few states of a discontinuum to all moving among many states of a continuum. On the basis of the Little Effect, the weak force is explained as a relativistic revolution (spinrevorbital) (correlation) of leptons about quarks for relativistics of Rule 2 and 3 as the electron motions and energies are as one moving relative to stationary quarks of discontinuum to all moving (e^- and quarks) among many states of a spinrevorbital continuum. The strong force has been evoked to explain the existence of the nucleus against the repulsion of like positive Coulomb charges of the protons of the nucleus. Here it is suggested that this strong force is actually an aspect of electromagnetic effects associated with the relativistic revolutions (correlation) of quarks to minimize their Coulombic repulsions. In the proton, such relativistic

revolutions of the up-quark about the other up-quark create magnetic attractive interactions to counter the electric repulsive interactions of the two quarks. According to Einstein (Einstein, 1918), acceleration is as a loss of mutual gravity (force). On the basis of the Little Effect, here it is suggested that the resulting acceleration from the relativistic quark revolutions (correlations) is equivalent to a loss of Coulombic electric repulsion of the two quarks. The two up-quarks in their mutual relativistic revolutions (spinrevorbitals) also relativistically revolve about the down-quark. This is consistent with Rosenzweig's theoretical quark confinement as a chromomagnetic Meissner Effect (Rosenzweig, 1984). On the nuclear scale, two protons exhibit relativistic revolutionary motions such that the down-quark is accelerated to the second proton and the second proton releases its down-quark of the other proton so there are complex revolutionary motions which confine the quarks to the two protons with residual confinement of the protons. The relativistic effect associated with the spinrevorbital motions by the Little Effect explains the mass-energy equivalence and such changes during nuclear and chemical transformations. Birnair (Birbrair, 1971) also hypothesized a coriolis antipairing theory for nuclear rotations by Meissner Effect. On the basis of the Little Effect, here it is suggested that the relativistic revolutions (correlations) of the quark fractional charges in their spin-magnetic fields are the source of the gluon! It is on this basis that the Little Effect explains neutron instability and proton stability.

The structure of the neutron is likewise of the proton's structure, but the neutron structure involves the mutual revolutions (correlations) of two down-quarks to overcome their electric repulsion with the further revolutions (correlations) of the down-quark pair about the up-quark. The proton can transform to a neutrons via capturing an electron. But the capture of the electron would involve it associating with an up-quark. On the basis of the Little Effect, here it is suggested that the association of the electron with the up-quark is the basis of what is called the weak interaction. The Little Effect suggests that this weak interaction is actually relativistic revolutions (correlation) (spinrevorbital) of leptons about the up-quark. According to the Little Effect, the relativistic revolutions (correlations) of the electron charge and spin about the up-quark (color) charge and spin causes an electro-weak interaction that forms the down-quark. On the basis of the Little Effect, during the reverse beta process such relativistic revolutions (correlations) of the electron about an up-quark within the proton causes the up-quark to form a down-quark which then undergoes transformation in revolutions so it revolves about the other down-quark of the nucleon rather than its prior revolutions about the remaining up-quark. The two down-quarks now revolve (correlate) each other to glue together and mutually revolve (correlate) about the up-quark to form the neutron. This process of reverse beta

between an electron and a proton requires revolutionary (momental) changes of the electron and quarks of the protons. These revolutionary (momental) changes are complex and cause the low cross-sections of reverse beta and the need for neutrinos for such processes. The complex momenta processes of the reverse beta on the basis of the Little Effect explain why bare neutrons are unstable yet bare protons are stable. Such effects are consistent with Fermi's realization of the ghostly neutrino particle (Fermi, 1934). Such effects are also consistent with the observed handedness of the weak interaction (Yan, 1979). On the basis of the Little Effect, here it is suggested that extremely strong magnetic field can cause increased cross sections for reverse beta. These extreme magnetic fields exist in neutron stars and magnestars (Jones, 2005). On the basis of the Little Effect, magnetic field can organize and influence the electron-quark and quark-quark correlations during reverse beta, nuclear fission and nuclear fusion processes. Many of these effects of electron and quark pair revolutions (correlations) in their mutual spin and charge fields to form lepton and quark revorbitals are demonstrated in this manuscript.

ATOMIC ELECTRONIC CONFIGURATION

Just as charge in motion and the resulting magnetism cause the internal structure of nuclei and nucleons, they also determine the structures of atoms. Electrons are Coulombically drawn to nuclei. Electrons also interact with each other in their mutual proximity to nuclei by Rules 1, 2, 3 and 4. These electron --- electron interactions cause the configuration of electrons into electronic shells, subshells and spinrevorbitals about nuclei. These electron – electron interactions include $e^- - e^-$ Coulombic repulsion and $e^- - e^-$ spin --- spin, $e^- - e^-$ spin --- orbital, $e^- - e^-$ spin – revolution, $e^- - e^-$ orbital – revolution, $e^- - e^-$ orbital – orbital, and $e^- - e^-$ revolution - revolution interactions. Electrons pair in orbitals because of their mutual attraction to the nucleus causes them to exist in a close state that overwhelms their repulsions. The pairing of electrons in orbitals against their Coulombic repulsions is further facilitated by the spin --- spin, spin – revolution, orbital – revolution, orbital – orbital, revolution – revolution, and spin --- orbital interactions within the electron pair, which leads to the spinrevorbitals by Rules 1-3. The Coulombic attraction of the electron pair to the nucleus causes their revolutionary (spinrevorbital) (correlation) motions about each other, which magnetically (relativistically) lowers their Coulombic repulsion by Rule 2. On the basis of the Little Effect, the electrons of the pair go into revolution (correlation) so as to create magnetic attraction and the relativistic loss of their repulsive Coulombic energy with their increase mass by Rule 2. Such effects of this proposed revolutionary motions bridge charge to spin and

mass. This pairing of electrons in orbitals is analogous to the pairing of quarks in nucleons. They are both caused by spin induced reorbital motions of charges on the basis of the Little Effect. On the basis of Einstein's (acceleration and force) equivalence such relativistic acceleration (Einstein, 1918) of the electron pair in their revolutions (correlations) diminishes their Coulombic repulsion. Here on the basis of the Little Effect, it is noted that even during chemical reactions nuclear effects and reactions occur although the energies are very minute. The pairing of electrons by the nucleus for a given shell number is greatest in the order: s orbitals > p orbitals > d orbitals > f orbitals. It is quite interesting that on this basis of the Little Effect that the correlations of electrons is time dependent based on the orbital motions of the electron pair about the nucleus with greater variation in the order: s < p < d < f ect... The Little Effect results in the electronic charge and spin in relativistic revolutions (correlations) (spinrevorbitals) about the charge and spin of the other electron causing magnetic interactions and relativistic effects that stabilize the pairing so the two electrons can be in a state of proximity near the nucleus. Within the atom, the electrons of shells, subshells, orbitals and revolutions manifest various phasal ($v < c$) (discontinuum) dispersions and group ($v > c$) (continuum) dispersions of $e^- \text{---} e^-$ spintransorbitals, $e^- \text{---} e^-$ nuclear spintransorbitals, $e^- \text{---} e^-$ spinrevorbitals and $e^- \text{---} e^-$ nuclear spinrevorbitals.

MOLECULAR ELECTRONIC CONFIGURATION

Just as the charge in motions and resulting magnetism cause internal structures of atoms and nuclei, they determine the structures and bonding in molecules. In molecules, electrons are Coulombically pulled to multi-nuclei structures. The electrons interact with each other in their mutual Coulombic attractions to many nuclei. Electron – electron interactions cause the electrons to configure into molecular orbitals with various symmetries (σ , π , δ ect...) in molecules by Rule 2. The electrons pair in molecular orbitals in spite of their mutual repulsion due to their $e^- \text{---} e^-$ spin --- spin interactions, $e^- \text{---} e^-$ spin -- revolutionary interactions, $e^- \text{---} e^-$ orbital – revolutionary interactions, $e^- \text{---} e^-$ orbital – orbital interactions, $e^- \text{---} e^-$ revolutionary – revolutionary interactions, and $e^- \text{---} e^-$ spin --- orbital interactions. The electrons pair in the molecular orbitals because their attraction to the multi nuclear centers overwhelms their Coulombic repulsion. On the basis of the Little Effect, electrons pair by their mutual relativistic revolutions (correlations) (spinrevorbitals) so as to create magnetic attraction and relativistic effects that overwhelm their Coulombic repulsions so they may exist closer to the multi-nuclear centers by Rule 2. The mutual attractions to the nuclei cause the $e^- \text{---} e^-$ pair to revolve. The Coulombic attractions of the two electrons to the nuclei cause their

relative rotation. The strength and energy of the revolutionary spinrevorbitals depend on the Coulombic attraction to the nuclei with greater acceleration of revolutions by greater effective nuclear charge from the centers by Rules 1 and 2. The $e^- \text{---} e^-$ pair revolutionary correlations (spinrevorbital motions) lowers their $e^- \text{---} e^-$ Coulombic repulsions by the consequent induced magnetic attractions and relativistic effects. On the basis of Einstein (Einstein, 1918), such accelerations in their revolutions diminish their Coulombic repulsions such that the repulsive Coulombic energy is transformed to spinrevorbital motions and mass. In the molecules by their mutual fall (accelerations in revorbitals) the electrons lose their Coulombic repulsion and bind magnetically and gravitationally. It is on this basis that magnetism and even gravity can affect molecular chemical reactions. The vibrations of nuclei in molecules (spintransorbitals) thereby modulate the electron spinrevorbitals and modulate magnetic and gravitational binding of the electrons in MOs by Rule 2. Thereby in molecules heat can bind electrons magnetically and gravitationally by Rule 2. Heat can perturb such many spintransorbitals into relativistic group dispersions (continuums) with many such phonon formed continuums strongly interacting to accelerate many spintransorbic and spinrevorbic relative motions for transforming surrounding heat into internal magnetism of excited spinrevorbitals and vice versa. For larger perturbations by pushing or pulling molecules together or apart many spintransorbitals can be excited into phasal dispersions (discontinuums) with many such interactions accelerating many spintransorbic and spinrevorbic phases and motions for transforming surrounding pressures and mechanical energies into van der Waals and London interactions via fractional charges in L frames interally and manifesting work and bulk mechanical energy in C frame. The relativistic revolutionary (correlational) (spinrevorbital) motions of the pairing electrons are accelerated by the multi-nuclear centers. It is important to note that the dynamics of such multi-nuclear pairing /unpairing of electronic spintransorbitals and spinrevorbitals occur at lower temperatures for low massive nuclei such that very novel effects of multi-hydrogen atoms and protons are observed at lower temperatures even room temperature relative to such dynamics for heavier nuclei. Such acceleration by multicenter nuclei (phonons) can explain superconductivity in the molecular structures. On the basis of the Little Effect, chemical bond rearrangement therefore involves nontrivial spin, revolutionary correlation, orbital and magnetic dynamics and relativistic effects although minute. It is on this basis that the Little Effect explains pycnonuclear phenomena, wherein in the bosonic pairs of spinrevorbital motions of electrons and protons (under acceleration by the lattice nuclear centers) form neutrons. Multi-nuclear centers accelerate electrons into and out of revolutions of pairing into molecular

orbitals. The electron correlations involve electron revolutions. The electron correlation and revolutions are stronger in σ bonds than π bonds and is stronger in π bonds than δ bonds. It is on this basis that the Little Effect determined that external magnetic fields lower temperature for breaking π bonds of C, N, O, and Si and delta bonds of Fe and Mo (especially in homogeneous atmospheres and magnetic fields) for causing diamond formation and other novel syntheses. The dynamics and kinetics of chemical reactions are determined by these aspects of electron correlation into pair bonds. On the basis of the Little Effect, the magnetic field can organize and influence the electron correlations during chemical bond rearrangements. Many of these effects of electron pair revolutions (correlations) in their mutual spin and charge fields to form molecular revorbitals are demonstrated in this manuscript.

BRONSTED-LOWERY ACID-BASE REACTIONS

The reaction dynamics of Bronsted-Lowery acid-base reactions are in accord with the Little (Effect) Rules such that spin effects of protons induce electronic orbital dynamics (spinrevorbital) on bases for the ready bond breakages for the ionization and the acidity of strong acids (HCl , H_2SO_4 , HNO_3 , and HClO_4) and the ready bond formations of protons (and other acids) to strong bases (CH_3^- , NH_2^- , OH^- and OR^-) by the efficient electronic rehybridizations during these bond rearrangements by spin induced effects of the entering protons (and other acids) according to the Little (Effect) Rules on the diamagnetically revolving electron pairs of the Bronsted-Lowery bases (Little, 2003) for novel processes by Rule 2 relative to prior interpretation of Rule 3. By the Little (Effect) Rules, the proton spins induce important electronic revorbital dynamics for important new kinetic factors by Rule 2 in addition to the underlying electrostatic thermodynamic driving force by Rule 3. On the basis of the Little Effect, the proton is a unique nuclear center based on the spinrevorbital nature of its 1s state (by Rule 2) and nuclear proximity. On this basis, the proton is active not only in pairing the electrons into bosonic covalent bonds (by Rule 2) but also and more so in providing a countering spin effect that disrupts the bosonic pairing of electrons (by Rule 2) of the covalent bond by magnetism, heat and gravity. It is this basis for hydrogen's unique chemistry and catalysis and its unique nuclear phenomena at lower temperatures even down to room temperature. Such paradoxical Coulombic binding and spin disruptions of covalency lead to the special solvency, importance and properties of water. On this kinetic basis of the Little (Effect) Rules, acidic solutions provide catalytic environments for facilitating many aqueous reactions even of monumental importance in the biosphere and the geosphere. Such effects of acidic protons by the Little Effect may account for observed

influence of strong magnetic field on acidic solutions, the sensitivity of biochemical reactions to external magnetic field and even terrestrial magnetic fields and future novel biochemistry and biology by use of external magnetization. It is this basis that water plays a central physical role to life. The observed effects of protium and deuterium during acid catalyzed reactions of $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ by Madsen (Madsen, 2000) is evidence of the Little Effect. According to the Little Effect, spin dynamics of the protons allow electronegative effects so the electron pairs are pushed out (by diamagnetic repulsions) from the protons with the acceleration of the electron pairs into new orbital states on the newly forming weak Bronsted Lowery weak base (Y^-) for $\text{H}^+ + \text{Y}^- \leftrightarrow \text{HY}$ by Rule 2. The Little (Effect) Rules account for the different acidities of HY and DY (Kresge and Allred, 1963). On this basis, important proton transfer dynamics are accounted for by the Little (Effect) Rules.

These spin induced revorbital effects also resolve the dilemma of classical versus nonclassical accounts of the hydrogen bond. Classically (Besnainou, 1988), the hydrogen bond is conceived as electrostatic effects of a dipole – dipole interaction that causes binding as in $\text{X} - \text{H} - \text{Y}$ by Rule 3. But nonclassically, the H bond has been modeled considering the nature of orbitals and the resulting molecular orbitals by Rule 2. On the basis of the Little Rules, the nonclassical (Briegleb, 1944) perspective of H bonding is enhanced due to the proton spin causing the needed spinrevorbital dynamics of two electron pairs (bosons) by Rules 2 and 3. The two electron pairs may condense about the proton for Bose-Einstein condensation about the positive charge. The correlated electron pairs are Coulombically attracted to the proton but simultaneously, diamagnetically pushed away from the proton spin. Here the Little Effect suggests a tautomeric effect of the proton on the two electron pairs from the two hydrogen bonded bases. The proton Coulombically and efficiently pairs the electrons for correlation into bonds, but the proton also pushes the bosonic pairs away (diamagnetically). This type of Coulombic pairing and diamagnetic repulsion on the basis of the Little Effect provides a basis for tautomerism by Rule 2. It is nontrivial here that the novel phenomena of the spintransorbitals and spinrevorbitals of the proton itself in interaction with spintransorbitals and spinrevorbitals of the $e^- \cdots e^-$ pairs cause and account for novel dynamics like tautomerism and superconductivity. The bosonic electron pair condensation may involve 2s, 2p frontier revorbitals of the proton as well as the 1s spinrevorbitals. The H-bond thereby involves a 3 centered, 4 electron bond. The electron repulsion may cause a state wherein the 4 electrons of the H-bond exist with 2sp bonding revorbital and 2sp antibonding revorbitals for zero bonding and an electrostatic interaction.

The complicated chemistry of water clusters (Keutsch and Saykally, 2001) is further evidence of these unique

proton spin induced revorbital mechanics for bonding kinetics by Rule 2. Such aspects of the Little Effect in water clusters and phases have been manifested in high pressure high temperature water (Moore et al., 2005). The bonding in hydrogen cluster ions (Buyvol-Kot et al., 2005; Eters, 1973) and the fleeting existence of these molecules also involves important spin induced revorbital dynamics based on the Little Effect. By the Little Effect, such fleeting clustering of water may explain and distinguish the liquid state from solid ice and gaseous steam. Bridge bonds and banana type bonds of hydrogen with boron in borides (Sass et al., 1997) are manifestations of proton spin induced revorbital effects on the bonding. The (4c,2e) bonding in $\text{Li}_4(\text{CH}_3)_4$ and (3c,2e) bonds in $\text{Be}(\text{CH}_3)_2$ and $\text{Mg}(\text{CH}_3)_2$ are weaker aspects of this spin induced orbital effect of 2s orbital of Li and Be and 3s orbital of Mg relative to 1s orbital of H. It is here that the Little Effect determines a crucial correlation of spin and orbital and revolutionary (spinrevorbital) dynamics of chemical bonds with superconductivity as the p^+ vibrations magnetically and gravitationally bind the revolving electrons together for superconductivity. Likewise in MgB_2 , Mg can bridge bond boron as hydrogen does but Mg has 3s electrons that can be excited into boron's hybrid conjugated states by spin induced revorbital processes that cause superconductivity at lower temperatures by Rule 1. Furthermore, the Mg center is less able at lower temperatures than hydrogen to spin disrupt the bosonic pair of superconductivity associated with the bridged boron structure. On this basis (in analog to MgB_2) in analog to MgB_2 , borohydrides, hydrocarbons, amino and hydroxides groups in various molecules and materials may under various conditions manifest multiproton (and multinuclear) induced accelerations of π electrons for induced spinrevorbitals of the pairs for loss of Coulombic repulsions of the many electron pairs for gain in magnetism and mass for magnetic and gravitational binding the pairs for novel superconductivity and physicochemical dynamics in such materials. The chemical shift of proton NMR (Linowski et al., 1976, Kumar and McAllister, 1998) is evidence of the ability of proton spin to influence electrons in spinrevorbital motions and vice versa. The distinct chemical and physical properties of ortho and para hydrogen (Ilicca et al., 1996; Andreani et al., 1998) are also evidence of the Little Effect. The mass isotope effects of protium, deuterium and tritium during chemical reactions (Capponi et al., 1999) have spin effects according to the Little (Effect) Rule.

LEWIS ACID- BASE REACTIONS

Within the general frame of the Lewis acid/base definition, the Little (Effect) Rules also provide kinetic bases for reactions in terms of Lewis acids providing spin

effects for revorbital dynamics (spinrevorbitals) of accepting the electron pairs from Lewis bases. This effect is exhibited in some isotopes of boron (Ambartsumyan, et al., 1974; Taylor et al., 1969; Brownstein, 1980). With its nuclear spin moment boron allows spin induced revorbital dynamics by Rule 3 for their kinetics of electrophilicity and Lewis acidity of boron compounds. On the basis of the Little (Effect) Rules, these spin induced revorbital dynamics (spinrevorbital) in boron compounds explain the high temperature superconductivity in magnesium diboride (Kotegawa, 2001; Nagamatsu, 2001; Slusky, 2001; Choi et al., 2002; Monteverde, 2001) as motions of nuclei modulate electron pair revorbitals to lower their Coulombic interactions and induce magnetic and gravitational binding in their motions for superconductivity as will be considered more below. Furthermore, the Little (Effect) Rules account for the decreasing Lewis acidity down the boron group and the inert pair effect for Tl (also Pb and Bi). In general, on the basis of the Little Effect the heavier atoms down the groups need less catalytic effects due to the weaker effective nuclear charges on their Fermi levels and weaker internal atomic spin exchange associated with their various bonding modes (at least for families prior to the carbon group where there after π bonding becomes important) by Rule 1. The lesser need for catalytic intervention for heavier congeners is a result of the weaker internal atomic spin exchange of electrons via the nuclei of the heavier atoms by Rule 1. The heavier atoms down the group have to greater uptake of thermal energy as the many nuclei accelerate electrons into revorbitals of lesser Coulombic repulsion and greater magnetic and gravitational binding for lowering thermal disruption of quanta and superconductivity at lower temperatures relative to frontier spins of less massive elements due to larger uptake of thermal energy and transformation of thermal to electric, gravitational and magnetic energies. Internal atomic spin exchange with impact on revorbital motions is strongest for boron and diminishes from Al to Ga to In to Tl. The stronger spin exchange for the lighter congeners leads to kinetically more difficult self-spin induced rehybridizations in boron relative to the heavier congeners. By the Little (Effect) Rules, the weaker spin induced revorbital interactions contribute faster internal rehybridizations of Tl^{3+} to Tl^{1+} for a magneto-electronic kinetics contributions and explanations of the inert pair effect and efficient disproportionation reactions of heavier congeners.

This kinetic explanation of the relative ease of rehybridizations of revorbitals based on internal spin effects by the Little (Effect) Rules also explains different high pressure induced electronic rearrangement of Ge, Si and carbon (Baidakov et al., 1996; Pohl and Pollock, 1986; Morita, 1974) such that Ge and Si more easily undergo high pressure induced metallic transformations but diamond does not on the basis of Rule 1. On the basis of the Little Effect and Rules, high pressure causes more atom --- atom interactions with consequent spin ---

spin interactions that contribute to easier reorbital rehybridizations in Ge and Si but difficult rehybridizations of reorbitals in diamond due to the prior mentioned stronger effective nuclear charge and stronger internal $e^- - e^-$ exchange of the lighter carbon by Rule 1. On the basis of the Little Effect, the greater effective nuclear charge of carbon causes greater correlated motions of electron pairs in the bonds and the inability to break the correlations as in Si and Ge for metallic phases for motions by Rules 1 and 2. The temperature must be raised at the higher pressures to break the correlation in the carbon thereby causing paramagnetic liquid carbon of density greater than diamond. By such the Little Effect has explained the liquid state of diamond and such possible states within the cores of planets like Saturn, Jupiter, Neptune and Uranus. Via the carbon nuclei, the electrons of 2p experience much stronger exchange interactions. The relative difficulty in high pressure metallizing diamond also follows from carbon being described by Russell Saunderson coupling whereas Ge and Si are more described by jj coupling. These kinetic explanations by the Little Rules further apply to the lone pair effects of Pb and Bi with the underlying thermodynamic driving force of greater effective nuclear charge of the Tl, Pb, and Bi due to the emergent effects of the lanthanide series. These explanations provided by the Little Rules account for the metastability of Tl^{3+} , Pb^{4+} , and Bi^{5+} and their tendency to disproportionate. The novel properties of many bismuth containing materials relative to counter parts antimony and arsenic are explained. It is interesting to here consider the effect of raising pressures in the new Ferrochemistry, Laws and Rules as presented here. Increasing pressure well beyond terrestrial pressures with higher temperatures has the (special) relativistic effect of greater transforming heat to work and work to electric energy on macroscale (C-frame) by exciting many relativistic phasal spintransorbitals in L frames and their stronger collective interactions for net charging in L frame (discontinuums) rather than fractional charging (continuum) in L frames as manifested and emerging collectively on larger scales in the C frame from a multitude of L frames. At even higher pressures and temperatures a general relativistic effect occurs of transforming the heat, work, electric energies of macroscale (C frame) to gravity by many general relativistic group spinreorbital excitations and macroelectric by bending many phasal spinreorbital excitations. Such effects of extreme pressures and temperatures on transforming heat, work, macroelectric energies, gravitational energies and macromagnetic energies give a new mechanism and theory for chemical bond rearrangements and novel properties like liquid crystallinity of diamond as in these planets of Saturn and Jupiter.

SUPERCONDUCTIVITY

Here it is predicted that such facile asymmetric orbital

dynamics of these heavier p block congeners provide explanations to superconductivity at low temperatures. (Later it is reasoned that mixing the superconductivity of these heavier p block materials with lighter p block materials raises the critical temperature (T_c) for superconductivity as manifested in many complex polyanionic, mixed-cationic layered structures). The first observation of superconductivity in Hg at low temperature (de Haas et al., 1925) is evidence of this account. The position of Hg in the periodic table and its electronic configuration is consistent with it being the first observed superconductor. Hg has a special electronic configuration such that it has frontier reorbitals of s, p, d, and f symmetries with filled 6s, 5d and 4f subshells such that 6s and 5d electrons may be rehybridized into sdp orbitals and excited by phonon induced spinreorbitals. The larger mass of Hg nuclei also contributes to its ability to superconduct and the first observation of superconductivity in Hg by Onnes in 1911. The larger effective nuclear charge (of Hg relative to Cd) due to the lanthanide effect (Zhang et al., 2002) and the 5d series also contribute important nuclear Coulombic attraction of frontier electrons for pairing electrons into relativistic spinreorbital states and exchange/correlations of such states by Rule 2 that can withstand low temperatures (and phonon/nuclear vibrations) associated with superconducting Hg. Below this superconducting temperature, bosonic electron pairs may be excited by vibrating Hg nuclei as relativistic spinreorbitals into delocalized, continuum unstable states by Rule 2; wherein the spinreorbitals rapidly, reversibly release the phonon to relax back to the superconductive bosonic pairs. This reversible phonon scattering into unstable, continuum spinreorbital states by Hg and p block elements during superconductivity by Rule 2 differs from the more irreversible scattering into the high density of stable discontinuum states within the d block elements during Ohmic conduction (metallic) by Rule 3. Unlike the high density of discontinuum, stable states of d block metals by Rule 2 and the scattering into nearby continuum like states by Rule 3 (which allow for longer lived excited stationary states for other phonon, magnon dynamics that lead to breakage of $e^- - e^-$ spinreorbital), the lower densities of discontinuum states with higher densities of intervening unstable, continuum modes by Rule 2 (in Hg and p block materials) result in greater probability of reversible phonon scattering (by massive Hg nuclei) from discontinuum and into continuum, unstable spinreorbital states by Rule 2 (which relativistically do not allow time for other phonons or magnons to further disrupt the spinreorbitals before they relax back to the superconductive spinreorbitals) and consequent magnetic and gravitational binding of superconducting fermions within such continuum spinreorbital states by Rule 2. The more massive Hg nuclei consume more thermal energy at higher temperatures for exciting this continuum, unstable

continuum, unstable spinrevorbital states of superconductivity at the T_c of Hg. The d block metals and their higher density of discontinuum stable states and lower nuclear masses facilitate phonon inversions about these lower energy phonons (for creating phonon inversions for an internal laser within the solid metal), which provides intense coherent, correlated phonons that easily irreversibly disrupt bosonic spinrevorbital states of superconductivity in d block metals with breakage of superconductive modes, ejection of superconductive electrons into the sea of electrons and dissipation of superconductivity to heat such that these d block metals require much lower temperatures and maybe higher pressures to avoid internal phonon lasing for superconductivity due to their masses and d frontier orbitals in the transition metals by Rules 1-3. However, the p block materials have lower densities of stable, discontinuum modes with the consequence of higher energy phonons to match their discontinuum modes of stable spinrevorbitals by Rules 1-3. Hg has empty 6p orbitals for exciting to manifest such attributes of p superconductivity but at lower temperatures. Indeed, it is reasoned here that Cd and other elements and materials of the 5th series may use their filled s and d orbitals to excite p block states for superconductivity at higher temperatures but in the past such superconductivity in pure elements has not been due to their shorter lifetimes; the lanthanide effect for Hg may extend the life time of its superconductivity relative to Cd and Zn. The heavier p block elements and Hg use large thermal energies in exciting their electrons into such superconducting continuum, spinrevorbital states. The p block materials therefore require and allow higher, greater kinetic energies (higher temperatures) to invert their phonons for phonon amplifications and stimulated emissions so as to provide intense, coherent, correlated phonons that are needed to disrupt the superconductive spinrevorbitals in these p block materials relative to d block materials by Rules 2 and 3. Also the p block materials would involve phonon conversions about continuum rather than discontinuum states (as in partially filled d bands of metals), such that the phonons of the continuum states in p block materials may enhance binding and organizations of the superconductivity by gravity and magnetism between the moving spins. Such organization of phonons and phonon inversions at higher required temperatures by p block materials may explain the role of heat baths in cuprates for raising superconductivity temperatures as the p block materials maintain temperature gradients at higher temperatures to sustain phonon organizing continuum spinrevorbitals in the superconductive phase. On the basis of the Little Effect, here it is predicted that inhomogeneous temperature gradients may interfere with phonon inversion and allow higher temperature superconductivity in metals by Rule 2 and the phonon inversions and lasing about continuum states in nonmetals may assist higher temperature superconductivity.

The phonon scattered, superconducting spinrevorbitals may undergo revolutionary dynamics, orbital rehybridizations and changes in spin. In order $d < p < s$, the revolutions and orbitals are subject to spin frustrations and spin induced dynamics such that the higher temperature superconducting phases of p block materials exhibit more magnetic intermediates relative to d block materials by Rule 1. The fall of the fermions in relativistic revorbitals in these continuum modes also causes their loss of Coulombic repulsions, increase their masses and induce magnetic and gravitational binding of their pairings into superconductivity for p block materials. The phonon scattered spinrevorbital states of p block materials are likely to undergo spin changes to develop fermionic pairs from the superconducting bosonic pairs by Rule 2. The stronger electron exchange in p block materials relative to d block materials allows for correlations of the scattered fermionic pairs by Rule 1. On the basis of the Little Effect, these high spin intermediates of p block materials may by spin induced rehybridizations to reform the delocalized bosonic superconducting modes by Rule 2. Therefore the superconducting spinrevorbital of delocalized, discontinuum states may be scattered by higher (relative to d block) energy phonons into unstable, continuum spinrevorbitals in p block materials, which rapidly relativistically relax back to the superconducting mode by Rules 1 and 2. Changes in multiplicity of the spinrevorbital upon its phonon scatter in these p block materials cause fermionic pairings with consequent high spin induced revolutionary dynamics and rehybridizations back to the delocalized superconducting modes. Above the T_c (although higher T_c in d block materials), the p block superconductors and scattered into continuum spinrevorbitals (by Rule 3) of momenta that exceed their gravitational and magnetic binding so the binding energies are converted to heat and the coupling of the continuum spinrevorbitals to the heat and phonons are diminished (by Rules 1 and 3). Therefore the lower azimuthal quanta of p block relative to d block materials favor superconductivity at higher temperatures with lower principle quantum number raising the magnetic, gravitational binding and heavier nuclei transforming more of the surrounding thermal energy into such gravito-magnetic binding for synergistic effects of frontier orbitals of lighter p block elements and more massive nuclei of heavier elements in these complex mixed heavy cationic polyanionic superconducting materials.

Since Onnes' discovery, superconductivity in Hg has been observed in other materials even at higher temperatures (Hatfield, 1988; Larouche and Datar, 1987; Meyer, 1963; Hermon et al., 1974). On the basis here of the relative strength of spin induced orbital dynamics for various elements, the Little (Effect) Rules predict future higher temperature superconductivity discoveries in Ga, In, Ge, Tl, Pb, Bi, In, Sn and Sb wider gap compound semiconductor materials. Even higher temperature

superconductivity is predicted in carbon, sulfur, phosphorus, silicon and nitrogen, germanium and arsenic compounds. Gua-meng Zhao and Beeli, report hot superconductivity in multiwall CNT (Zhao and Beeli, 2005). Zhao's observations and other observations of 2p elements (Zhao and Beeli, 2005) are consistent with the Little Effect.

Some of these effects are consistent with the Dresselhaus Effect (Ganichev, 2005; Wang et al., 2005) and the Rashba Effect (Governale, 2002; Kravchenko and Rasha, 1971) in materials like InAs/GaSb (Hoffman, 2005) and InSb/GaAs (Poghosyan and Demirjian, 2003; Hoffman, 2005). But the Little Effect and Rules differ from the band edge splitting of Kramer pair states by the two mechanisms of the Dresselhaus Effect and the Rashba Effect. The Little (Effect) Rules differ in that the Dresselhaus Effect involves excited orbitally induced spin effects (bulk inversion asymmetry) during electrical conduction in these materials. The Rashba Effect involves band-edge voltage induced asymmetric transition (structure inversion asymmetry). The Dresselhaus and Rashba Effects focus on how the orbital motions affect spin of conduction electrons. However, the Little Effect and Rules involve many spins and how motions of spins cause revorbital dynamics. The novel effects associated with the Dresselhaus Rule and the Rashba Rule follow from these compounds formed from p block elements wherein phonons scatter more nonclassically by Rule 2 relative to phonon scattering of electrons in d block metals by Rule 3. Furthermore as already considered for p block atoms, the internal spin exchange in p block elements is greater relative to d block atoms by Rule 1. A mix of s, p, and d orbitals allows for more order of electronic motions in L frames in coupling with lattice motions in C frame, including spin ordering by motions into different revorbitals during conduction and scattering. Moreover a mix of orbitals and interacting spinrevorbitals and nuclei on light p block elements and heavy d block elements (respectively) allow combined benefits of stronger excitations and gravitomagnetic binding by less massive p block spinrevorbitals and greater thermal soaking and transduction to gravity and magnetism by more heavy d block nuclei in the complex compounds. Many important spintronic devices now result from these effects (Johnson, 2005).

On the basis of the Little (Effect) Rules, here it is demonstrated that the first observed superconductivity by Onnes in Hg involves the spin induced revorbital dynamics available by 6s, 5d, 6p, and 4f revorbitals for this Hg element with the frontier orbitals of Hg allowing phonon exciting empty p block spinrevorbitals for superconductivity and the heavy nuclei of Hg transducing the low thermal energies of C frame to the continuum electronic states of L frames with gravitomagnetic binding for the superconductivity. At the extremely low temperatures, Onnes was able to observe a superconducting phase in Hg wherein low energy phonons

scatter electron pairs into high spin excited hybrid continuum states by Rule 2. The stronger spin exchange and mass between the excited electron pairs of p block atoms cause resilience to classic phonon scattering and resilience to the resulting classic phonon induced losses of correlated, coherent motions. Phonon motions of high spin, excited states by the Little (Effect) Rules cause efficient revorbital rehybridizations and relaxations to superconducting bosonic pair correlated states. The Little Effect causes the high spin scattered pairs to efficiently relax by spin induced revorbital rehybridizations back to the bosonic superconducting states. For consistency, on the basis of BCS theory (Bardeen et al., 1957), phonons may scatter electrons into these orbitals wherein Dresselhaus and Rashba Effects may cause high spin scattered states. The Little effect would involve high spin induced scattering back into the superconducting modes.

HIGH TEMPERATURE SUPERCONDUCTIVITY

The Little Effect accounts for high temperature superconductivity. The Little Effect with Kasha Rule (Kasha, 1963) and El-Sayed Rule (El-Sayed, 1963; Shimakura et al., 1977) predicts for the HOMO-LUMO states reversible phonon induced excitations of superconducting electron pairs by Rules 1 and 2 into orbitally induced high spin excited states by Rule 2 for Fermi pairing of the resulting excited pair with the reversible asymmetric relaxations (Little Effect) back to boson pairings of the superconductive states by Rule 2. By the El-Sayed Rule, the excitation into LUMOs may contribute orbitally induced spin transitions and changes in multiplicity. By the Kasha Rule, the electrons rapidly relax to the lower levels. The relaxations to lower vibronic high spin states by Kasha Rule and El-Sayed Rule further involve spin induced revorbital rehybridizations (Little Effect) for relaxations from these high spin states according to the Little (Effect) Rules (1 and 2) to the low spinrevorbital states that reform the bosonic superconducting pairs. This mechanism involving phonon scattered bosonic and fermionic pairs (for triples) for explaining superconductivity is consistent with recent discoveries of E. Demler (Demler et al., 2004) of triplet superconductivity and others observing fermionic superconductivity (Shopova, 2005; Machida, 2001). Here it is important to note how these effects of Kasha, El-Sayed, Dresselhaus and Rashba in conjunction with the Little Effect are more feasible in the p-block semiconductors due to the better balance between stronger spin exchange of p revorbitals relative to d revorbitals and the greater revorbital extension of p revorbitals relative to s revorbitals (by Rules 1-3). For higher temperature superconductivity, by Rules 1-3, the e^-e^- pairs must be more strongly bound to the nuclei as in lighter p block elements and the thermally scattered states must involve higher energy group dispersions for gravitational binding and/or phasal dispersion for

macromagnetic binding the scattered superconductive states. The electronic structure of Hg is consistent with this perspective due to the ready availability of s, p, d, and f as frontier revorbitals of Hg and the electronic structure and massive nuclei of Hg corresponds with the first observed superconducting phase being observed in Hg (de Haas et al., 1925).

The feasibility of these electronic states (s, p, d) is related to the inherent electron-electron interactions and electron-nuclei interactions and natures of s, p, d and f type revorbitals with multiplicity of electrons. The currently observed high temperature superconductivity in complex structures like CeMn₅ (Daniel et al., 2005), PuMgAs₅ (Daniel et al., 2005), CePt₃Si (Frigeri et al., 2005), Sr₂RuO₄ (Kaur et al., 2005), CeCoIn₅ (Rourke et al. 2005), Na_{0.5}CoO₂ (Balicas et al., 2005), TeBa₂CuO₆ (Kobashi et al., 2004), and LaBaCuO₄ (Klingeler et al., 2005) is supportive of the explanation here. These complex structures involve atoms with these various assessable s, p, d, and f frontier revorbitals. These complex structures also involve nuclei of various masses so that massive nuclei and their greater ability to soak up thermal energy and couple the thermal energy into excited continuum superconducting electronic states of not just their own frontier states but frontier continuum states of lighter elements, which have stronger magnetic and gravitational binding of the continuum superconductive modes for causing the observed higher temperature superconductivity in these complex structures. The s subshell provides greater electron --- nuclear exchange and nuclear Coulombic interactions by Rule 1. The p subshell has less exchange and nuclear Coulombic interactions with its electrons with more revorbital extension and faster electronic motion relative to the s revorbital by Rules 1 and 2. The d subshell provides even lesser exchange and nuclear Coulombic interactions of its electrons relative to the p revorbitals with greater electron --- electron interactions of d revorbitals relative to p revorbitals due to more orbital extension and faster electronic motions by Rules 1-3. The f revorbitals are under stronger revorbital motions and exchange with less extensions than the d revorbitals. As a result, the s, p, d, and f revorbitals in pure metals (of the d and s block) exhibit Ohm's conductivity with HDOS phonon assessable conductive discontinuum modes with efficient classic scattering of electrons by phonons (by Rule 3) and weaker binding of these conduction electrons (spinrevorbital) by the weaker spin interactions and the weaker gravitational interactions due to the weaker electron exchange in the d block metals by Rules 1 and 2. In essence, this reflects the greater polarizability of heavy d block metal atoms relative to heavy p block metal atoms. As previously noted the effective nuclear charge has an important influence on the pairing and exchange energy of frontier electrons and the consequent spinrevorbital properties for superconductivity and the temperature, pressure conditions of superconductivity by

Rule 1. Mn, Fe, Co, and Ni exhibit exceptions to this weak exchange of d block metals because the localization of lone electrons and Coulombic integrals are larger for these metals (Lambert and Hendrickson, 1979; Garifullina et al., 1972) so their Cooper pairing is not applicable. On this basis, high pressure may increase orbital overlap for stronger nuclear --- electron pairing in these ferromaterials for superconductive phases that scatter by phonons reversibly into strongly coupled fermionic or bosonic pairs (by Rules 1 and 2). Such explanations by the Little Effect and Rules explain the recently observed superconductivity in HPHT Fe (Shimizu et al., 2001). Such effect of pressure on orbital overlap has been observed in other materials like cadmium chalcogenides (Il'ina, 1985), Xe (Yakovlev et al., 1979), (Huang et al., 1982) and even elemental materials (Shimizu et al., 2005).

The s block metals have weaker overlapping revorbitals and fewer electrons than p and d block materials. The heavier p block metals involve the more efficient use of p revorbitals for superconduction, wherein the exchange between electrons via nuclei is greater and the Coulombic interactions with the nucleus is greater relative to d block atoms by Rule 1. The p block metals may also hybridize with s and d revorbitals for novel band structures and resulting physicochemical effects. On the basis of the Little (Effect) Rules, the s, p, d hybrid conduction electrons by Rules 1 and 2 may undergo spin induced promotions and rehybridizations among these various states. These states of p block elements have lower densities of discontinuum states relative to d block metals so the electronics are more nonclassical on the basis of the quantum approximation by Rules 1 and 2. Furthermore, the stronger Coulombic interactions of p block frontier electrons cause less stable intermediary continuum states and stronger magnetic and gravitational binding and transductions of these continuum states by Rules 1 and 2. The greater instability and internal binding (magnetically and gravitationally) of the continuum modes of p block relative to d block materials cause less probable destructive scattering and uncorrelation of superconductivity by Rules 1 and 2. On the basis of the Little Effect, here it is suggested that these hybrid superconducting and phonon scattered states include π bonds, conjugations and resonances and possibly aromaticity on larger length scales, which contribute to the superconductivity. On the basis of the Little Effect, these orbital differences with spin inductions in p block metals and their compounds relative to d block metals and their compounds give better explanation of the p block fractional quantum Hall effect (Schwarzschild, 1998) relative to the integer quantum Hall effect (Landwehr, 1985) in d block metals, respectively. The fractional quantum Hall effect in confined semiconductors is a result of its p type frontier revorbitals which exhibit lower densities of states and much stronger e --- nuclei interactions and e --- e exchange interactions for stronger

bosonic and possibly fermionic pairings relative to the integer quantum Hall type d block metals by Rules 1-3. This stronger electron interactions of p block cause more liquid-like conduction electron phases by Rule 1. However, the d block metals exhibit much weaker Coulombic and exchange effects to their conduction electrons thereby the conduction electrons behave more like gassy phases by Rules 1 and 3.

The greater exchange and Coulombic interactions between electrons in p subshell lead to stronger bound bosonic and fermionic interacting pairs (triples) by Rules 1 and 2. Such stronger e^- --- nuclear interactions and e^- -- e^- interactions via nuclei for the p block elements and their compounds contribute greater binding (magnetically and gravitationally) and stability of correlated states relative to those of the d block by Rules 1-3. Here it is suggested based on the Little Effect that such stronger interactions will eventually lead to even higher temperature superconductivity. This prediction is demonstrated by the observed superconductivity in CNT with magnetic scattered phases (Zhao and Beeli, 2005). The stronger coupled bosonic and fermionic pairs (triples) for the p-block materials cause more liquid like behavior of conduction electrons for fractional quantum Hall Effects by Rule 2 relative to the gassy phase behavior of electrons of more weakly interacting d block metals by Rule 3, which exhibit the integer quantum Hall effect. These stronger interacting bosons and fermions (triples) in p block materials are here predicted to contribute to higher temperature superconductive phases by Rules 1-3. In general on the basis of the Little Effect, the lattice is bound by electron pairs that are correlated as revolving pairs of electrons so as to magnetically oppose their Coulombic repulsions. In such revolutions of the electron pairs, they lose their Coulombic repulsion in their falling (accelerating) (revolving) and they gain magnetic binding and increase weights for gravitational binding of their superconductivity. The lattice nuclei pair, revolve and correlate (spinrevorbital) the electronic bosonic pair. Phonons or lattice vibrations cause the electron pairs to correlate to oscillate rhythmically between stable discontinuum (by Rules 2) and unstable transient continuum spinrevorbital (by Rule 2) states in orchestration to lattice vibrations of phonon inversions. Such use of lattice thermal energy and phonons to excite the electronic pairs of bosons and fermions use more thermal energy for more massive nuclei and the resulting continuum superconductive spinrevorbitals are magnetically and gravitationally bound for higher temperature superconductivity. The oscillations in electron pair correlations involve changes in revolutionary (spinrevorbital) modes of electron pair. The Little Effect thereby demonstrates the reversible coupling of lattice phonons with correlating electron pairs of macro-delocalized conjugation, resonance, aromaticity and superconductivity.

Higher energy phonons cause greater compressions

and rarefactions of the electron revolutions (spinrevorbitals), which if strong enough can cause spin flip of the electrons with excitation of pairs into fermionic states. The resulting fermionic excited states (by Rules 1 and 2) of the electron pairs obey a different statistics, motions and structures relative to the ground state bosonic phases (by Rules 1-3). But the fermionic excited states still correlate the electron pairs. The fermionic excited coupled states can reversibly relax to the bosonic state by releasing phonons, but for the reverse, a change in spin multiplicity is required. The Little Effect allows such spin induced the orbital dynamics and spin asymmetry. On the basis of the Little (Effect) Rules, stronger the nuclei Coulombic field correlates the electron pairs as bosons or fermions for triples with stronger bindings with stronger coherence and organizations against higher energy phonons of higher temperatures. Also the more massive surrounding nuclei require more thermal energies in their vibrations with more corresponding transductions of such thermal energies into superconductivity continuum states for sustaining higher temperature superconductivity. On the basis of the Little Effect, the stability of the bosonic superconductive phases and their phonon scattered fermionic intermediaries depend on Coulombic interactions with the nuclei (lattice) and also the consequent exchange interactions between the fermionic pairs (by Rules 1-3). Higher temperature superconductivity will involve stronger bonds of the Cooper pairs and Demler pairs to the lattice with consequent stronger exchange. Here it is predicted that the light p block elements and their compounds will meet the higher temperature conditions for such super currents.

A great example of these revorbital effects of s,p,d, f and the spin exchange, spin polarizations, Coulombic binding to the lattice nuclei and nonclassical density of states is given by MgB_2 . Although MgB_2 does not involve d and f revorbitals, the frontier revorbitals include 2s and 2p of B and 3s and 3p of Mg of early orbitals. The bonds (spinrevorbitals) may be described as partly ionic and partly covalent. Here it is interesting to compare elemental superconductors with compound superconductors. In the elemental superconductors, the electric fields and phonons influence the spinrevorbital. In compound states, the spinrevorbitals are determined based on different electronegativities of the nuclei as well as electric fields and photons. In this compound case, the spinrevorbital involves states mostly associated with the more electronegative boron with various conjugations for delocalization of the spinrevorbitals. The bonding in Mg compounds has been known to lead to excellent thermal transport properties with poor electrical transport properties. Below 39 K, the phonons of MgB_2 are limited to nonclassically scattering the Copper pairs (by Rule 1 and 2) {associated mostly with polyanionic conjugated bonds of boron (B^{2-}) chains and sheets ($B-B=B-B=B-$

$B=B-B)^{n-}$ with attached $n/2$ Mg^{2+} ions for charge compensation } into coherent, correlated (spinrevorbital) high spin antibonding states $(B=B-B-B \cdot \dots \cdot B-B=B-B)^{n-}$ (by Rule 2) wherein $B=B$ π bonds are tautomericly broken and reformed along the chain into $(B=B-B-B \cdot \dots \cdot B-B=B-B)^{n-}$ high spin radical parts. The chain –sheet polymeric boron anionic structures involve polyanionic borons with Mg^{2+} cations to decoratively balance the charges along the boronic backbones or sheets. The 3s revorbital of Mg^{2+} cations allow 3 centered, 2 electron bond between boron anions. The Mg^{2+} cations by their thermal energies and phonons facilitate via their 3s revorbital the rehybridizations and bond rearrangement dynamic of boron's π bond rearrangements that are associated with superconductive modes by Rule 2. The Mg^{2+} cations allow tautomerism that cause superconductivity of excited π electrons along the polyanionic boron chain or sheet. Furthermore on the basis of the Little Effect, at low enough temperature the Mg acts as alkali and alkaline earth cations centers for crowns and crytates so as to shuttle spinrevorbital electron pairs in and out of its 3s revorbital to bridge B during superconduction. At below 39K, phonons scatter Cooper pairs of this π bonds by Rule 2 in this superconducting state into high spin $s^1p^1p^1p^1$ fermionic continuum states by Rule 3 $(B=B-B-B \cdot \dots \cdot B-B=B-B)^{n-}$ {El-Sayed Effect, Dresselhaus Effect, Rashba Effect}. In such high spin fermionic continuum based on the Little Effect phonons in conjunction with the $s^1p^1p^1p^1$ $(B=B-B-B \cdot \dots \cdot B-B=B-B)^{n-}$ high spin intermediary states (bind magnetically and gravitationally) readily rehybridize this high spin states back to the sp or sp^2 $(B=B=B-B=B-B=B-B)^{n-}$ superconducting state by Rule 2. At low enough temperatures, the weaker vibrations allow electrons of $s^1p^1p^1p^1$ revorbitals of $(B=B-B-B \cdot \dots \cdot B-B=B-B)^{n-}$ anions to cooperatively interact to reform hybrid sp , sp^2 revorbitals by rule 2. The weak vibrations (below T_c) of high spin $s^1p^1p^1p^1$ $(B=B-B-B \cdot \dots \cdot B-B=B-B)^{n-}$ units of the polymeric MgB_2 structure cause spin induced rehybridizations of the $s^1p^1p^1p^1$ to sp or sp^2 $(B=B=B-B=B-B=B-B)^{n-}$ hybrid revorbital states such that by resonance and conjugation along the chain, the anionic $B=B=B-B=B-B=B-B$ determine the superconducting state by Rule 2. Low densities of state and Pauli antisymmetry of the $s^1p^1p^1p^1$ $(B=B-B-B \cdot \dots \cdot B-B=B-B)^{n-}$ limit the phonon induced scatter of the high spin states into incoherent states by Rule 2. The large Coulombic interaction of the Cooper pair with the nuclei because of sp type revorbitals and the resulting large spin exchange, magnetism and gravity between carriers to stabilize the coherent correlated high spin scattered excited state thereby allowing their relaxations back to the correlated superconducting states with release of phonons or conversion of phonons to magnons and gravitons. Therefore the superconductivity is a delocalized high spin excited continuum states in MgB_2 structure facilitated by low temperatures wherein

vibrations reversibly scatter Cooper pairs into correlated high spin continuum states (spinrevorbitals) which relax back to the superconducting phases by Rule 2. Above the $T_c = 39$ K, the Mg cations via phonons excite the π superconductive electrons into dissipative dynamics by Rule 3. The observed diminished superconductivity of MgB_2 with Al doping is consistent with this delocalized polyatomic description of superconductivity (Slusky et al., 2001). Third row elements are less able to π bond than second row elements by Rule 1. Furthermore, the third row elements have weaker Coulombic interactions of Cooper pairs with nuclei and weaker spin exchange for polarizations of electron pairs by Rule 1. The innovation by the Little Effect is that the reversible scattering involves spin induced orbital dynamics with consequent rehybridizations and then the reverse spin induced revorbital rehybridizations. On the basis here of the Little Effect, superconductivity involves bond rearrangements and tautomeric chemistry of excited states. This is the first effective explanation of correlation and coherent scattering during superconductivity.

Here on the basis of the Little Effect, it is suggested that superconductivity is delocalized bonding effects on a macrolength scale. So on this basis, superconductivity involves delocalized hybrid (spinrevorbital) electronic states where in phonons excite transitions between these states and strong spin, magnetism and gravity by Rule 2 and revorbital exchange (of the resulting phonons scattered electronic states) induce efficient relaxations and transitions between these superconducting (spinrevorbital) hybrid states. Phonons can cause scattering from these superconducting hybrid revorbital states, but the lower density of states, the stronger electron exchange for pairing, rehybridizations and spin scattering (Little Effect), and the resulting spin polarized electron pair in the superconducting media, allow for higher probable reversible relaxations to the superconducting modes for p block compounds (by Rules 1-3). Revorbital effects during phonon scattered transitions cause spin transitions optically by El-Sayed Effect and during conduction by Dresselhaus Effect and Rashba Effect. The Kasha Rule allows efficient relaxation of higher energy phonon scattered modes to the lower energy modes of the spinrevorbital by Rule 3. On the basis of the Little Effect, the resulting phonon scattered states of high multiplicity and continuum cannot relax to nonsuperconducting modes because of antisymmetry by Rule 2. However by the Little (Effect) Rules, the resulting high spin states scattered continuum phases from the superconducting state can relax back to the superconducting discontinuum phase by spin induced revorbital rehybridizations by Rules 1-3. On this basis, the multiplicity of the scattered phase limits dissipative relaxations to non-superconductive modes. This theory of high temperature superconductivity on the basis of the Little Effect is consistent with observed low temperature superconductivity by BCS theory (Bardeen et al., 1957),

pressure induced superconductivity in some substances (Shimizu et al., 2001; Yakovlev et al., 1979; Il'ina, 1985; Shimizu et al., 2005) and the recent magnetic disruption (Steiner et al., 2005) of superconducting phases, magnetic and high pressure induced breakdown of superconductivity (Huang et al., 1982), high field (60T) abnormal states (Ono et al., 2004), and spin stripe phases of superconductivity in magnetic field (Steiner et al., 2005; Klingeler et al., 2005). The recent experimental observations of charged density waves, stripes, antiferromagnetism, twisted space and square density waves and rectangular density waves can be reasoned and even predicted from this prior model of the relativistic spintransorbital and spinrevorbital formations under varying conditions such that the heat is transduced to mechanical energy and pressure fields for rectangular phase by underlying motions ($v < c$) of many coupled L-frames for special relativistic organization of heat in C frame from the many coupled excited group dispersions (fractional charges) in L frames; and the mechanical energy is transduced to macroelectrical energy for square charged density phase by underlying motions ($v \sim c$) of many coupled L frames for greater special relativistic compression of space in the direction of motion for greater organization of heat in C frame from the many coupled excited phasal dispersions (integer charges) in L frames; and the electrical energy is transduced to gravitational energy for twisted phases by underlying motions in different directions of many L frames for general relativistic bending of space out of the direction of motion for greater organization of heat in C frame from the many coupled excited group dispersed (fractional spiral, orbitals and dipoles) in L frames; and the gravitational energy is transduced to macromagnetic energy for spiral phases by underlying motions and fall of heat under the gravities in C frame and fracture and coupling to broken orbitals of many L frames for general relativistic spiraling and pulsating in spiral for transforming space to time and time to space for greater organization of the heat in C frame from many coupled excited phasal dispersed (integer orbitals of L frames translated in C frame for orbital spiral structures) and mixed L/C frame with onset of superconductivity in C frame; and the macromagnetic energy is or can be transduced to orbital magnetism and energy for orbital phases and trapping by underlying motions and acceleration of heat and gravity in the C frame by macromagnetism in C frame (and possibly flipping bright and or dark gravities) and interaction and coupling to whole orbitals of many L frames for quantum general relativistic orbits and pulsations and revolutions of self-interactions by spatial transformation to internal time for greater organization of heat in C frame from many coupled excited phasal dispersed (integer orbitals of L frames trapped under their internal interactions within the respective L frames for toeing orbital structures and excited wavefunctions of discontinuums and transient

continuums) and L frames with magnetic disruption of macro-superconductivity.

On the basis of the Little Effect, these conditions of high pressure and external magnetic field on superconductive phases are understood and explained. The spinrevorbitals of the superconducting phases undergo ever-present phonon scattering into various excited, continuum spinrevorbital modes of the unstable, relativistic continuum with strong magnetic and gravitational binding of the fermions by Rule 2. But the relativistic coupling of the spinrevorbital cause rapid reformations of the lower energy superconducting modes. This relativistic effect of organized spinrevorbital motions for correlations has been seen by others as Meissner effect (Agassi and Oates, 2005; Bardeen, 1955; Schafroth, 1958; Decker et al., 1967). Under high pressure (Yanai et al., 2003) the higher atom – atom collision frequencies contribute high frequency rehybridizations of revorbitals and alterations of frontier band structures that can destroy or sometimes form superconducting phases. Strong magnetic external or intrinsic field may alter the Hamiltonian such that the scattered superconducting modes (spinrevorbitals) form either dynamic, virtual states of sufficient gravitomagnetic binding to sustain superconductivity by Rules 1-3 or the scattered superconductive modes may undergo change in multiplicities of the perturbative virtual continuum states of phonon scatter with the breakage of the superconductivity (by Rules 1-3). The high spin scattered state may also be superconductive depending on the exchange energy. On the basis of the Little Effect, the strong external magnetic field disrupts the efficient reversible transitions between the bosonic spinrevorbital phases of the superconduction and the high spin, scattered fermionic continuum spinrevorbital phases. The resulting high spin phases may cause revorbital rehybridizations in the external magnetic field with loss of π bonds and conjugations and resonance that cause the superconductivity.

COMPLEXES

In addition, here it is demonstrated that this effect of lone electrons on (spinrevorbital) dynamics by the Little (Effect) Rules account for the properties of transition metal complexes and many catalytic phenomena. The spin magnetic exchange between the unpaired electrons in d spinrevorbitals of centers in complexes and the spinrevorbital motions of electrons of ligands can induce spinrevorbital dynamics of the electrons of the ligand for the catalyzing ligand chemical transformations. In most transition metal complexes, the ligands act as donors by providing electron pairs (coordinate covalently) and not by providing lone electrons (regular covalent) to the metal center. Ligands with lone electrons may bind the lone electrons of the metal center for regular covalent

bonding. But even for these two types of ligands (the coordinate covalent type and the regular covalent type ligands), the metal centers {with lone electrons of d spinrevorbital symmetries, or even p spinrevorbital or f spinrevorbital symmetries (but less so) may via exchange interactions by these d spinrevorbital lone electrons} influence the electrons on the ligands according to the Little Rule 2 so as to affect the chemical transformations of the complex and the chemical transformations of the ligands. The Little Effect is most obvious (during such chemical and catalytic transformations of the complexes) when the metal center is a 3d atom and the ligands are either 3d, 2p, or 4f atoms. These type metal centers and ligands are under Russell Saunderson coupling and exhibit stronger spin polarizations and exchanges. The lone electrons on the metal center via exchange provide spin induced revorbital dynamics and rehybridizations of electrons of the ligands to facilitate bond rearrangements for binding entering ligands or pushing out leaving ligands by Rule 2. Such spin induced revorbital dynamics according to the Little Effect also facilitate chemical transformations of ligands.

These manifestations of the Little (Effect) Rules toward the kinetics of transition metal complexes are beautifully demonstrated by considering well known rates of water exchange. The oxygen of water is the donor atom and it is described by Russell Saunders effects. First of all, the s block ions, except the smallest (Be^{2+} and Mg^{2+}), are very labile toward aqua exchange. The lability of s block ions to water exchange is consistent with the Little (Effect) Rules, just as the proton and protolysis are consistent at higher temperatures. The s spinrevorbital (for p block and s block metals) allows the strongest interactions of ligand donor electrons to the nucleus of the metal centers for nuclear spin induced revorbital effects that facilitate ligand entering and leaving dynamics for lability by Rule 2. On the basis of the Little Effect, the nuclear spins by Rule 2 (of the metal center) or the protons (during protolysis in acidic media) perturb the motions of the electron pair by Rule 2 during the coordinate covalent bond rearrangement between the metal center and the ligands during the exchange reactions. The odd nuclear spins of the metal centers can induce discontinuum to continuum activation of lone electrons on the ligands with consequent facile bonding dynamics and rearrangement of ligands by Rules 2 and 3. Such nuclear spin induced spinrevorbital dynamics of s block and d block metals by Rule 2 to the contrary of the superconductivity of these elements relative to p block materials is here reasoned on the basis of the more local molecular scale of the complexes relative to more macroscale of the superconductivity. The s block also via exchange through the nucleus allows strong spin interactions of lone electrons of an atom.

The s orbitals also via such large exchange couple electron pairs of crown and cryptate ligands for their Bose-Einstein condensation around alkali and alkaline

earth cations. Most of the s block elements have odd numbers of protons and neutrons in their nuclei so the odd number of nuclear spins via efficient interactions with donor electron pairs of the ligands via the s spinrevorbitals allows the nuclear spin induced spinrevorbital changes by Rule 2 of donor electron pair to facilitate ligand exchange kinetics and cause lability. There are some alkaline earth cations with even number of nuclear spins and these correlate with slower exchange kinetics relative to Ba^{2+} and Sr^{2+} . Ba^{2+} has the fastest exchange rate, which by the Little (Effect) Rules may be explained by the greater number of neutrons to protons in its nucleus and the higher possible nuclear spin moments by Rules 1-3. This effect by the Little (Effect) Rules is different from the Buchachenko Effect of magnetic isotope effect (MIE) (Bernadskii et al., 2005). Whereas MIE considers nuclear magnetic spin exchange with electron spin with the antisymmetric prevention of chemical bonding, here the Little Effect involves the nuclear spin causing spinrevorbital changes of the electron for affecting the kinetics of chemical reactions. The Little Effect is different from the Buchachenko Effect (Bernadskii et al., 2005) or the radical pair effects of Stein (Steiner and Ulrich, 1989), Turro (Buchachenko et al., 1998) or Hayashi (Hayashi et al., 2001). The Little Effect is the first rule that reveals how spins transform revorbital motions and other spins so as to affect asymmetric chemical and physical transformations. Buchachenko (Bernadskii et al., 2005), Stein (Steiner and Ulrich, 1989), Turro (Buchachenko et al., 1998) and Hayashi (Hayashi et al., 2001) Effects do not involve these dynamical aspects of physical and chemical transformations. But by the Little Effect of different nuclear spins and statistics, it is here presented as previously proposed that isotopes of different bosonic and fermionic nuclei can be separated based upon their different induced spinrevorbital changes of donor electron pairs for different ligand exchange kinetics and labilities. Such differences have been predicted and demonstrated by RBL for separating fermionic isotopes in graphene oxide membranes.

Furthermore, the Little Effect accounts for the kinetic trends in water exchange of aqua complexes of d block metals. M(II) cations of the first d-series exhibit moderate lability, which is accounted for by the Little Effect on the basis of the strong spin electron -- electron exchange of these metal centers with the electrons of ligands for accelerating donor electron pairs in and out of the metal centers. Although the 3d metal cations attract the Lewis base ligands electrostatically, their lone electrons present fermionic spinrevorbitals by Rule 2 that perturb the diamagnetic electron pairs of the coordinate covalent bonds by Rule 2 for facilitating kinetics of bond rearrangements. Furthermore, the observed effect that strong ligand fields on d^3 and d^6 metal centers of the first series exhibit inertness provides more excellent account by the Little (Effect) Rules because in the strong field the

lone electron pairs on the metal centers become paired losing their spin moments and consequent ability to induce spinrevorbital dynamics by Rule 1 and 2 of bond breakage and formation during ligand exchange at the lower temperatures of consideration. The stronger ligand fields thereby slow water exchange under the considered conditions. The consistency is further demonstrated by considering that d^{10} cations (Zn^{2+} , Cd^{2+} and Hg^{2+}) are also labile, which follows from their use of s spinrevorbitals just like the alkali and alkaline earth cations for faster ligand exchange dynamics. Considering the prior considered alkali, alkaline earth and group 10 cations, it is important to note that the Little Effect explains the great abilities of these cations to ligate cryptate and crown ligands based on the ability of their nuclear spins by Rule 2 and spinrevorbitals to push ligand electrons in and out of donors by Rule 2 of the crowns and cryptates with reversible Bose-Einstein condensations of the pairs with s spinrevorbitals about the metal centers. The observed trend that the 3d complexes with the largest ligand field stabilization energy (LFSE) exhibit more inertness is consistent with the explanation by the Little (Effect) Rules. The largest LFSE causes more pairing of electrons on the metal center by Rule 2 for less spin induced revorbital effects by Rules 1 and 2 for ligand exchange. The Little (Effect) Rule even explains the greater inertness of complexes with 4d and 5d metal centers relative to 3d metal centers by Rules 1 and 2. The 4d and 5d metal atoms have smaller internal electron --- electron exchange and spin polarization by Rules 1 and 2. The couplings of angular momenta of 4d and 5d metal centers are of the jj type rather than Russell Saunders type. Therefore spin induced effects for 4d and 5d transition metals are less forceful for changing spinrevorbital motions associated with ligand exchange. So aqua exchange reactions for 4d and 5d metal centers are slower. For completeness of this account, it is important to note that f block metal centers exhibit lability, which is consistent with the given Little Effect on the basis that their f spinrevorbitals are more buried and the exchange dynamics are determined by the 6s and 7s empty spinrevorbitals.

In considering these relative effects of water exchange in the various metal centers, it would be remiss if the self-exchange is not considered under higher temperature activating conditions to account for structural, chemical and physical properties of bulk and nanoparticulate metals and also the exchange of important ligands other than water, for example carbonaceous (organometallic) and nitrogenous ligands. The 3d transition metals would be weak field self-ligands of the Russell Saunders type with consequent smaller ligand field stabilization and higher , such large exchanges and spin polarizations result in the ferromagnetism of Fe, Co, and Ni by their self-ligations. Whereas for $M - (OH_2)$ with $M = Fe, Co, Ni$, the spin states by Rules 1 and 2. As previously considered

complexation involves 3d and 2sp type spinrevorbitals, the pure metals would involve weaker electron --- nuclear Coulombic and electron --- electron exchange interactions of M – M atoms with 3d spinrevorbitals. This causes weaker pairing of electrons into correlations by Rules 1 and 2 within Fe, Co and Ni such that they are unpaired for more fermionic spinrevorbitals and ferromagnetic properties. This comparison is consistent with the diminished ferromagnetism with carbon, nitrogen and oxygen dissolution into the bulk Fe, Co and Ni metals. The unusual lower melting temperatures of Fe, Co and Ni relative to other transition metals are explained on the basis of the lower activation energy for breaking M-M bonds due to the lone electrons of the 3d spinrevorbitals by Rules 1 and 2 and their disruption of bosonic spinrevorbitals by Rule 2 of the M-M bonds to melt the lattices. These effects as predicted by the Little (Effect) Rules also explain the unusual melting points of Fe, Co, and Ni and their carbides and nitrides (Braun, 1965). R.B. Little observed an unusual lowering of the eutectic temperatures of metals in hydrogen in strong magnetic field and explained this effect based on the Little (Effect) Rules by Rules 1 and 2. These differences in ligand binding to Fe, Ni and Co metal centers explain the lower melting of the pure metal in comparison to the carbides, nitrides and oxides. The unusually lower melting temperatures of the metals and their hydrides in external magnetic field are also explained by the Little Effect. The Little Effect also explains the unusual BCC structures of Fe, Co and Ni (al'perin, 1959). On the basis of anomalous low melting points and structural dynamics, RB Little realized unique catalytic properties of molten Fe, Co, and Ni relative to other transition metals. Just as for oxygen of H_2O , the liquid Fe, Co, or Ni exhibits labile exchange of carbonaceous and nitrogenous ligands, which facilitates the catalyses by these metals of reactions involving these atoms by Rule 2. These metals exhibit according to the Little Effect unique catalytic effects to C, N, O atoms due to the large spin polarizations and spin exchanges, which transform electron pairs by Rules 1 and 2 to lone electrons and high spin radicals by Rule 2 on the ligands containing C and N donors, for catalyzing the chemical rehybridizations of revorbitals and fixations of C, N, and O into higher bond order hybrid states for greater hybrid bond order by Rule 2. On the basis of the Little Effect, these ferrometals due to their lone electrons and consequent high spins disrupt the $e^- --- e^-$ correlations of the spinrevorbitals in bonds of the ligand atoms associated with π bonding in $C=C$, $O=O$, $N=N$. The lone electrons of the Fe, Co and Ni centers and the large spin exchange by Rule 2 of complexations disrupt the ability of C, N, and O atoms to correlate their electrons into pairs for π bonding by Rule 2. The unique ability of these ferrometals to catalyze formations of diamond, CNT and NH_3 is evidence of these unique dynamics of complexations and the consequent exchange, spin induced recorrelations of π

bonds of bosonic pairs by Rule 2 to non-bonded fermionic radical pairs by Rule 2. The 4d and 5d transition metal atoms exhibit weaker self-exchange and spin polarizations, so they are not ferromagnetic at the lower temperatures of consideration by Rules 1 and 2. Furthermore, the 4d and 5d transition metals have higher densities of discontinuum stable states that facilitate the kinetics of trapping ligands into metastable bound states. The 3d Fe, Co and Ni metals have lower densities of discontinuum states by Rule 2 and higher density of unstable continuum states by Rule 3, such that the unstable continuum states do not afford kinetics to trap ligands into metastable bonds Rule 2. Likewise 4f transition metals have weaker exchange in spite of the high spin per atoms so they are not ferromagnetic by Rules 1 and 2. For similar reasons according to the Little Effect, the 4d, 5d and 3f metals are not able to catalyze similar nitrogenous, carbonaceous and oxygenaceous reactions of ligands as do Fe, Ni and Co.

Now considering the ability of these ferrometals to uniquely ligate other Russell Saunders ligands like carbon and nitrogen donors, such unique ligations have been the basis of R. B. Little explaining diamond and carbon nanotube formations. Carbonaceous and nitrogenous ligands are under Russell Saunders coupling so they would interact favorably with Fe, Co, and Ni centers. The C and N bonds are strong so that under proper high temperature conditions the ferro-metals can catalyze breaking the carbon and nitrogen bonds by Rule 1. Such catalytic activity of Fe, Co and Ni in bond transformations of carbon and nitrogen according to the Little Rules would involve spin induced reorbital dynamics for rehybridizing the electrons of the carbon and nitrogen into complex states of high multiplicity and further spin induced reorbital rehybridizations by Rule 2 upon releasing the carbon and nitrogen atoms to various products. Such spin induced reorbital dynamics by the Fe, Co, and Ni on the carbon and nitrogen result in the accelerated, asymmetric transformations of the carbon and nitrogen into high spin electronics states by Rule 2. The resulting spin induced asymmetry slows the kinetics of chemical bonding back to reactant symmetries on the basis of Woodward-Hoffmann Rule (Woodward 1942, Hoffman and Woodward, 1972) and by Rules 1 and 2. Whereas the previously considered aqua complex transformations and catalytic activities occur at room temperature, these activities of Fe, Co and Ni on carbon and nitrogen donors require high temperatures by Rules 1 and 2. Under such extreme conditions, it is feasible to speak of inverted complexations wherein the 2p atoms are now the centers and the metal atoms are the ligands. During CNT formation Fe, Co and Ni nanocatalysts complex carbon with the lone electrons of these metals causing diminished ferromagnetism for spin density wave. This change in magnetic properties with carbon adulteration has been demonstrated experimentally (Yin et al., 2001; Yang and Dong, 2005).

The complexation of Fe, Co, and Ni by carbon also causes structural changes in the metal nanoparticles by Rule 2. The structural changes cause rearrangements with spinreorbital changes and resulting spin density dynamics. The resulting electronic, magnetic, thermal and structural dynamics of these metal centers associated with ligation by carbon atoms allow carbon to diffuse through the metal particles and on the surface of the metal particles. The processes by which the metals absorb/adsorb carbon, transports carbon and release carbon therefore involve electronic, magnetic, thermal and structural dynamics associated with complexations (Little, 2003). At the cooler regions of the catalyst, the carbon is released to graphitize under the electronics of the spin density wave. The Fe, Co, and Ni metal atoms via spin accumulations release carbon atoms into sp^2 hybrid spinreorbitals according to the Little Effect. Under higher pressures and high temperatures the ferrometals exist as ferro-liquid crystal medias that release carbon atoms into sp^3 hybrid spinreorbitals to form diamond rather than graphite by Rules 1 and 2. Unlike the low pressure low temperature solid Fe, Co and Ni catalysts, the high pressure high temperature liquid catalysts of Fe, Co and Ni retain spin order and ferromagnetism such that the metal centers orderly and concertedly release high spin carbon atoms to higher order sp^3 hybrid bonds (Little, 2005). Hydrogen atoms in these medias provide added spin with the lone electrons of the d spinreorbitals of the catalysts to induce spinreorbital dynamics for sp^3 hybrid release of carbon atoms to the growing diamond lattice according to Rule 2. The high pressure high temperature (HPHT) induced ferromagnetism (Makarova, 2003; Gauzzi et al., 2003) of the catalyst also creates a dense state of bonding (the compressed state allows more exchange for magnetism) and exchange with the forming diamond so as to stabilize surface carbon radicals to prevent π bonding and graphitization. Here it is important to note that the Little Effect again employs the Meissner Effect on the subatomic scale for bond transformations between sp^2 graphite and sp^3 diamond. The high pressure high temperature induced ferromagnetism in the metal-carbon media and the high spin has a larger impact on disrupting π (spinreorbital) bond formation than the disruption of σ (spinreorbital) bond formation by Rule 1 (for a Meissner Effect) such that the magnetic field disrupts π bosonic bonding and correlations more readily with less consequent magnetic field effect on the stronger σ bosonic bonding and correlation by Rules 1 and 2. It is important to consider the different magnetic field strengths and their impact on π and σ bonds by Rule 1. Stronger external magnetic fields are needed to disrupt σ (spinreorbital) bonds relative to the fields needed to disrupt π (spinreorbital) bonds by Rule 1. It is on this basis of the Little Effect that different magnetic field strengths cause different kinetics of σ bond and π bond rearrangements and transformations by Rules 1 and 2. It is also on this basis that R. B. Little

discovered (Little, 2005) diamond formation in strong magnetic field (15T) with dramatic distinction from Druzhinin and coworkers (Druzhinin et al., 1988) a decade earlier. Druzhinin and coworkers (Druzhinin et al., 1988) applied ultrastrong pulsed magnetic fields (several hundred tesla) to diamagnetically compress graphite on the basis of old HPHT themes for forming diamond. The ultrastrong magnetic pulses of Druzhinin and coworkers (Druzhinin et al., 1988) affected both kinetics of π as well as σ bond formations. However, Little (Little, 2005) applied weaker magnetic field of steady duration for affecting mostly the π bond formation so as to discriminate and select diamond crystallization and prevent graphite formation. The ultrastrong magnetic fields of Druzhinin and coworkers provided the diamagnetic compression for forming diamond but the size was not much different from the older mechanical methods of HPHT synthesis. Druzhinin does not realize the lower field selectivity to σ over π bonding, but Little does discover selectivity.

On the basis of the Little Effect, the π bond exhibits more unstable discontinuum states by Rule 1 and 2 whereas the σ bond exhibits more unstable continuum states by Rule 1 and 2. The higher energy of discontinuum modes of the π bonds provides easier kinetics of disruption of the π bond relative to the σ bond. Unlike the π bonds, the σ bonds involve stable discontinuum spinrevorbital modes that relativistically, rapidly relax back upon perturbations, which make them thermodynamically more difficult to break. The σ spinrevorbitals are less labile relative to the π spinrevorbitals. The beauty of Little (Little, 2003) is that the growth rate, quality and size of the lower pressure steady field synthesis of diamond is much improved relative to older the arts of Hall and Derjaguin. Similar effects occur with the catalytic transformation of N_2 and H_2 to NH_3 by the Haber process. The HPHT conditions of the catalyst induce ferromagnetism of the catalyst for creating an exchange by Rule 2 with the N and H atoms to stabilize N and H radicals until they can bind for NH_3 to desorb and protons and lone electrons in d orbitals of the catalysts also disrupt $N=N$ π bonding and transform sp and sp^2 N to sp^3 N via spin induced revorbital rehybridizations. In considering the catalytic roles of Fe, Co, Ni in both graphene, carbon nanotube and diamond and $N_2 + H_2 \rightarrow NH_3$ syntheses, it is important to note the novel ability of the spintransorbitals of these catalyst in the L frames to readily (by special theory of relativity via thermal and mechanical energetic perturbations from the C frame) form hidden group dispersed spintransorbitals (fractional charges) in the L frame (to organize and synchronize heat of the C frame into mechanical, macroelectric and quantum energies) and to form phasal dispersed spintransorbitals (integer charges) in the L frame (to organize and synchronize thermal and mechanical energies of C frame into macroelectric and quantum electric energies). It is further important to note

the novel abilities of spinrevorbitals of these catalyst in the L frame to readily (by general theory of relativity via thermal, mechanical and electric energetics perturbations of the C frame) form hidden group dispersed spinrevorbitals (fractional orbitals and fractured orbitals and spiral unraveled orbitals) in L frame (to organize and synchronize heat, mechanical and electric energies of L frame into bright and dark gravitational energies and to form phasal dispersed spinrevorbital (whole orbitals and macro-spiralled orbitals in time and fractured orbitals of monopolar gravities) in L frame (to organize and synchronize thermal, mechanical, electrical and gravitational energies of C frame into macromagnetic and quantum magnetic energies). Such abilities of these Fe, Co, and Ni ferromagnetic catalyst to transduce thermal, mechanical, macroelectric, gravitational and macromagnetic fields and energies of C Frame into quantum electric and quantum magnetic energies and fields by Rules 1 and 2 explain the abilities of these catalysts to efficiently focus, synchronize and organize their energies for catalysis of huge numbers of these high energy chemical bonds in the C frame. Also on the basis of these transductions, the effects of higher temperatures, higher pressures, electric fields, gravitational fields and accelerations and magnetic fields on the catalysis and chemistries can be rationalized.

FERROMAGNETISM

Ferromagnetism exists in a few metals like Fe, Co, Ni and Gd (Hubbard, 1979). Some elements exhibit novel ferromagnetic effects on the nanoscale and in alloys (Zuckermann, 1971; Zhou et al., 2002). The Little (Effect) Rules account for this ferromagnetism. The Little (Effect) Rules explain the intrinsic ferromagnetism of Fe, Co, and Ni and induced magnetism in other substances. On the basis of the extension of revorbitals and the 3d subshell, spin induced revorbital motions (Little Effect) of 3d electrons facilitate hybrid states with 4s and 4p revorbitals with the consequent reduced 3d extension and localized lone electrons in 3d revorbitals for unpairing spins for magnetism of the atoms with the consequent inherent ferromagnetism via exchange interactions in clusters, nanoparticles and bulk Fe, Co, and Ni by Rules 1 and 2 (Lambert and Hendrickson, 1979; Garifullina et al., 1972). The consequent higher spin induced revorbital states according to the Little (Effect) Rules lead to the 3d revorbitals falling lower in energy than the 4s revorbital with the bonding via spd revorbital hybridizations causing such exchange for the spin correlations between atoms and the consequent ferromagnetism by Rules 2 and 3. The pairing energy associated with the chemical bonds of Fe, Co, and Ni metal atoms is much greater than the splitting energy due to effects of the Little (Effect) Rule whereby the parallel spins of electrons cause Pauli antisymmetry with fewer covalent bond and lower

electronic repulsion due to the spin interactions of the electrons forcing them further apart in reorbital motions thereby lowering their Coulombic repulsions. For such lower splitting energies of metals centers like Fe, Co and Ni with ligands, the metal centers and ligands have insufficient effective nuclear charge over the molecular orbital to pair the electrons thereby causing the fermionic reorbital states by Rules 1 and 2. The resulting higher splitting energy and higher pairing energy from the spin induced reorbital effects cause the lower bond order and ferromagnetism due to the exchange via the fewer bonds formed between atoms of Fe, Co and Ni. Such spin induced hybrid bonding with lone unpaired electrons in accord with the Little (Effect) Rules lowers the energy of the Fe, Co, and Ni relative to higher bond order states with fewer unpaired electrons of lower spin and magnetism by Rule 3. The spin polarizations and exchange energies are so great that the trends in bond structures and properties of Fe, Co, and Ni are anomalous relative to other transition metals. In addition to the unusual ferromagnetism, other anomalies include unusual melting points, carbide properties and hydride properties of Fe, Co and Ni relative to other transition metals (Braun and Kohlhaas, 1965; al' perin, 1959; Buschow and de Chatel, 1980). The greater extensions of 4d reorbitals relative to 3d reorbitals and the greater $e^- \cdots e^-$ repulsions of 4d result in the diminished spin induced hybrid bonding by the Little (Effect) Rules in 4d transition metals by Rules 1 and 2. These predictions and explanations of the Little (Effect) Rules are consistent with the observed magnetic properties of some nano-size 4d metals which have no ferromagnetism in bulk sizes. The surface tension and compression on nanoscale compress 4d reorbitals for novel spin effects associated with radical electrons on the surface and novel nanoscale magnetic order. The emergence of the lanthanide series contributes different effects of greater electronegative for more pair bonding in 5d transition metals relative to the prior noted effects in 3d Fe Co and Ni. Another important consequence of the Little (Effect) Rules is the observed properties of the lanthanides and the actinides. The huge spin induced reorbital motions in lanthanide atoms cause even greater localizations of 4f electrons relative to 3d electrons such that the 4f electrons are buried beneath 6s and 5d subshells (Jorgensen, 1985) by Rules 1 and 2. The Little (Effect) Rules here accounts for the nature of the lanthanides and their chemical similarity. This effect of spin induced reorbital effects is diminished for 5f actinides due to the greater $e^- \cdots e^-$ repulsions, which causes greater protrusion of 5f reorbitals and greater chemical diversity of actinides. For completeness it is interesting to compare elements of 2p subshell (B, C, N, O, F, Ne) with the 3d and 4f elements. The 2p reorbitals do not extend as much as 3d reorbitals so the 2p reorbitals bonds are stronger covalent bonds (as with 5d transition metals) relative to 3d and 4f covalent bonds by Rules 1 and 2. The energetics are such that the

pairing energy is small relative to splitting energy and strong interactions of 2p electrons with nuclei causing stronger covalent bonds relative to bonds involving 3d and 4f reorbitals by Rules 1 and 2. Spin induced reorbital effects are therefore not as important in 2p elements as in 3d and 4f elements under ambient conditions. However Little has determined exotic conditions for unveiling the spin induction of reorbital dynamics and rehybridizations in 2p elements by Rules 1 and 2. Because of the huge splitting energies and strong covalent bonds of 2p atoms, on the basis of the Little Effect the bosonic electron pairs experience huge effective nuclear charges for tight correlations and binding of the electrons, which causes more relativistic effects by Rules 1 and 2. The strengths of the spinreorbitals are much greater than those of the bonds of 3d metals. Therefore much greater magnetic fields are needed to directly disrupt the spinreorbital of 2p covalent bonds relative to 3d covalent bonds by Rules 1 and 2. R. B. Little has employed higher temperature and hydrogen atmospheres to lower the needed external magnetic field for disrupting the spinreorbital of the 2p covalent bonds thereby modulating their chemical transformations by Rules 1 and 2. For example, the novel ferro-metal solvating (or H atom solution) environments cause important spin induced reorbital effects on the basis of the Little Effect in 2p elements (Little, 2003; Little, 2005) by Rules 1 and 2. This novel ferro-liquid crystal environment is in accord with the Treatise on Resolution of the Diamond Problem by Little (Little, 2005). High pressures and high temperatures can also cause conditions of 2p elements where in spin induced reorbital dynamics affect chemical reactions and properties (Little, 2004) in accord with the Little (Effect) Rules by Rule 2. The Little (Effect) Rules thereby account for paramagnetism and the metallic nature of liquid carbon phase and the liquid carbon metal being denser than diamond (Bundy, 1980) by Rule 2. The Little Effect on the basis of the greater $e^- \cdots$ nucleus Coulombic interactions for stronger bonds and greater $e^- \cdots e^-$ exchange via the nuclear interactions predicts that light 2p and 3p elements and their compounds will determine important superconductive structures even above room temperature by Rules 1 and 2. Here it is suggested that sulfur under high temperatures and high pressures will exhibit such technological useful superconductivity.

The consideration here and comparison of 2p, 3d and 4f elements on the basis of the Little (Effect) Rules account for various catalytic natures and physicochemical properties of H_2 , H_2O , CH_4 , FeH and GdH species, mixtures and compounds. The H atom is able by spin induced reorbital rehybridizations to affect orbital dynamics for various bonded states in these materials by Rule 2. As a result of its spin induced reorbital dynamics, H is the most unique element. It is very interesting to point out the unique spin induced reorbital dynamics of the H atoms and the proton (on the basis of

the Little Effect) to account for such observations and phenomena as keto-enol tautomerism (Yamabe et al., 2004; Hass et al., 1996). The Little (Effect) Rules perfectly explain such efficient rearrangements by the ability of the protons via spins to efficiently drive revorbital rehybridizations on the oxygen, α carbon and β carbon for $sp^2 \leftrightarrow sp^3$ rehybridization dynamics associated with the tautomerism.

FERROMAGNETISM IN 2P ELEMENTS

The Little (Effect) Rule also accounts for chemical changes in various 2p structures associated with beta irradiation, proton irradiation (Esquinazi et al., 2004; Talapatra et al., 2005) and neutron irradiation (Mita et al., 1997). The electron, proton and neutron are fermions, which can cause spin induced revorbital dynamics under proper activating conditions by Rule 2. The recent observations of radiation induced ferromagnetism of nanodiamond (Talapatra et al., 2005) and graphite (Yaguchi et al., 1999) are evidence of protons causing bond breakages and the resulting exchange causing the resulting diamond to couple spins for ferromagnetic properties of the diamond by Rule 2. Electron irradiation of depositing carbon and its induction of diamond nucleation (Sokolowski and Sokolowska, 1982) are additional evidence of the ability of fermionic irradiation of carbon allotropes to cause spin interactions that promote revorbital rehybridizations according to the Little (Effect) Rules by Rule 2. Neutron irradiation for the production of color centers in diamond (Dutov et al., 2003; Mita, 1996) and other gems is a further example whereby spin interactions of neutrons alter spinrevorbital electronic states for optical changes by Rule 2. Intense laser irradiation has led to ferromagnetic states of carbon known as carbon nanofoam (Mattis, 2005; Gamaly, 2000). On the basis of the Little (Effect) Rules, Little has discovered novel neutron induced changes in some materials (Little, 2003). On the basis of the Little Effect, the spin associated with these irradiations by fermions cause disruptions in revorbital correlations of electrons that break bonds and quench the resulting radical impurities into different states by Rule 2. For consistency, on the basis of the Little Effect these novel spinrevorbital effects in carbon materials have led to observed superconductivity in polycrystalline diamond and CNT.

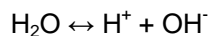
The Little Effect has already considered how superconductivity involves excited bosons in delocalized chemical bonds, which by phonons scatter into reversible spinrevorbital states including fermionic states. On the basis of the conjugation, ferromagnetism and exchange in carbon allotropes, it is not surprising that these allotropes under proper conditions exhibit superconductivity.

ELECTROCHEMISTRY IN EXTERNAL MAGNETIC FIELD

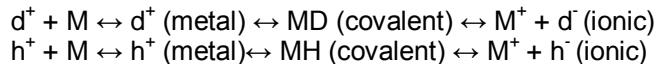
The H atoms within some transition metals are spectacular phenomena that have not yet been understood. The Little (Effect) Rules provide explanations and understanding. Various hydrogenous phenomena within transition metals such as high absorption (Tanaka et al., 1981; Gelatt et al., 1979), catalytic properties (Harouin et al., 1988; Xhang et al., 2002; Fujii and Okamoto, 1984; Buschow and de Chatel, 1980), isotopic separation (Fujii and Okamoto, 1984; Fujita and Garcia, 1991; Baird and Schwartz, 1999; Rodkin et al., 1999; Kaur and Prakash, 1982), absorption-expansion effects (Saito et al., 1997) and pycnonuclear fusion (Yakovlev et al., 2005; Sekerzhitskii and Shul'man, 1980) have been pondered controversially. The Little (Effect) Rules provide bases for understanding these great mysteries. The weaker but yet important spin induced revorbital dynamics in 4d transition metals relative to 3d transition metals has been noted here and this explanation on the basis of the Little (Effect) Rules accounts for the greater uptake of H atoms by late 4d transition metals like Pd and Ag. The higher electronegativity of these metals allows the ionization of H and the existence of higher concentrations of protons within the metal lattices as suggested by Mott (Perrot and Dharma-Wardana, 1984). On the basis of the Little (Effect) Rules, here it is suggested that spin induced revorbital dynamics cause pycnonuclear fusion phenomena (Little, 2005). Such remnant of spin induced revorbital states on the basis of the Little Effect result in unique catalytic activity of hydrogen desorbed from certain transition metals by Rules 1-3. The desorbed hydrogen from the metal exhibits unique catalytic activity relative to hydrogen unexposed to the metal (Podgorny et al., 1993) by Rule 2 and 3. Unlike 3d metals, the 4d metals (in particular Pd) have higher H absorption due to stronger bonding interactions of H with the lattices relative to bonding between metal atoms of 3d transition metals by Rules 1 and 2. For a metal like Pd, the large uptake of H is so much with consequent stronger covalent and ionic lattice interactions by protons and deuterons that mobility is high and the confinement of protons and deuterons can occur within the Pd lattice by Rules 1 and 2. Here based on the Little Effect, it is suggested that the properties of rapid transport and confinement of hydrogen are a result of the tautomeric oscillations between ionic and covalent bonding between hydrogen and Pd lattice (respectively) by Rule 2. The efficient s-d-p revorbital rehybridizations of Pd and spin dynamics of associated paramagnetic states are important aspects of the covalent-ionic bond fluctuations by Rule 2. Unlike 3d metals, 4d metals possess both important spin and orbital couplings with consequent important spin induced rehybridization effects within the Pd lattice by Rules 1 and 2. Pd and H ions facilitate such spin induced revorbital dynamics. The

faster transport of d^+ (boson) relative to p^+ and t^+ (fermions) is an aspect of differing spin induced reorbital interactions of lattice electrons with the different hydrogen isotopes on the basis of the Little Rule by Rules 1 and 2. The different isotopes also exhibit different confinement effects on the basis of spin induced reorbital effects.

Many of these phenomena of H atoms in late transition metals have been observed by R. B. Little with the Cu-Ag coils and the cooling water in strong DC resistive magnets. The DC resistive magnets employ high volt and high current to generate strong magnetic fields up to 33 tesla. Such high currents generate huge heat loads that must be removed by ultrapure cooling water in order to ensure operation and prevent overheating of the magnets. The resulting Cu-Ag -- H₂O interface under such extreme catalytic surrounding, electric field, magnetic field, temperature fluctuations, and high pressure provides a remarkable environment for predicting and observing some novel effects by Rules 1 and 2. It was predicted that this environment provides conditions for shifting the water autoionization:



The shift was predicted on the basis of the Little Effect due to the uptake of hydrogen by the coils to form metal hydrides by Rules 1 and 2.



Little observed high levels of hydrogen within used Cu-Ag magnet coils by SIMS. Furthermore, Little observed anomalously high deuterium/protium ratios in the used Cu/Ag coils relative to unused Cu-Ag coils. The high levels of hydrogen were attributed to the reduction and uptake of hydrogen from the water by the metal coils. The high d^+/h^+ is thought to be due to different spin effects of electron transfer between the metal and protium ions vs deuterium ions of the cooling water by Rules 1 and 2. Pycnonuclear fusion of absorbed hydrogen (e^- , p^+) to form neutrons may also be a reason by Rule 2. This whole mechanism of water decomposition is consistent with O₂ formation within the cooling water. The complete reduction of the hydrogen of the water would form O anions, which can react with the metals to form oxides or react to form O₂ (g). It has been determined that an extended coil lifetime occurs if a nitrogen blanket exist over the cooling water tank. Here it is suggested that this N₂ blanket (rather than the atmosphere) removes the generated O₂ during this H₂O magneto-electro-chemical decomposition. The observed build-up of black Ag₂O on the used coils is also consistent with this view. The cooling water was observed to be stripped of deuterium on the basis of isotopic analysis. Slightly higher levels of ¹⁸O/¹⁶O were measured in the recycled cooling water. In addition to the magnetic field effect on the relative h^+/d^+ uptake, the magnetic field effects on the relative Cu/Ag

oxidations and dissolutions by Rule 2 were measured. It was observed that increased magnetic field increased and influenced Cu and Ag oxidations by the water by Rules 1 and 2. The magnetic induced oxidation effect was greater for Ag than Cu such that the Cu/Ag concentration ratio in cooling water decreased with increased magnetic field from 30T to 45T by Rules 1 and 2. This is consistent with the greater d^+ uptake with stronger magnetic field. The reduction of h^+ or d^+ from the cooling water requires e^- transfer from the Cu-Ag metal to the h^+ or d^+ . In stronger magnetic field, the e^- of the metal and the nucleus of h^+ are spin polarized. d^+ has zero spin for a bosonic nucleus and no consequent polarization in the external magnetic field. So in order for the e^- to transfer to the h^+ , the e^- spin must flip its spin. Ag is more able (relative to Cu) via spin induced reorbital effects to internal intersystem cross its electrons in order to transfer its electron to the h^+ by Rules 1 and 2. So Ag is more readily oxidized than Cu in the stronger polarizing external magnetic fields. Since d^+ has no spin, e^- transfer to d^+ is less dependent on magnetic field strength. This is one explanation of the accumulation of d^+ in the Cu-Ag coils.

It is important to note that for zero magnetic fields, Cu has both thermodynamic and kinetic advantages for undergoing oxidation relative to Ag. So it is quite remarkable that above 30 Tesla the Ag oxidation increases relative to Cu. This remarkable observation is explained by the Little (Effect) Rules. Being of the 3d series, Cu has more internal spin exchange than Ag, so the electrons of Cu are more easily and strongly spin polarized for affecting the electron transfer to H⁺. Ag is more characterized by jj coupling whereas Cu is more characterized by Russell Saunders coupling. The stronger external magnetic field magnetizes Cu so as not to allow its electron to flip for electron transfer to the proton for the aqueous oxidation of Cu by Rule 2. Ag on the other hand, having spin-orbital coupling frustrates the spin forbidden transition due to s-d orbital flipping of electron spin by Rule 2. These analyses of both the Cu-Ag coils and the cooling water of the magnet provide consistent results. Extremely high levels of hydrogen were observed in the Cu-Ag metal as a result of being in aqueous environment and in the strong magnetic field for prolong times by Rules 1 and 2. The metals become more brittle with exposure to strong magnetic field for long times. The brittleness and hydrogen absorption by metal have been observed by others (Kolesnikov, 1996). On the basis of Little (Effect) Rules, the spin induced reorbital effects on the uptake of deuterium and the oxidation of Cu and Ag in the strong magnetic field are supportive of such spin reorbitals effects in pycnonuclear fusion.

THERMO GRAVITATIONAL MAGNETO FUSION

The Little (Effect) Rules have cosmic significance,

providing many new explanations for fusion phenomena in stars, for supernovas, for neutron star formations and for blackhole formations. It has been stated that magnetic fields shape the universe (Vlemmings et al., 2002). The internal structure and dynamics of our sun and other stars are determined not only by gravitational, strong, electric, weak forces/energies and thermal energy. Here it is suggested that the magnetic fields in such environments also contribute immensely to stellar structures and stellar dynamics within these stars. Under stellar conditions of huge mass densities and strong gravities, atoms are ionized as remarkably the huge gravity causes macrosystems to behave by Rule 2 rather than Rule 3. Under such extreme thermal, mechanical, electrical, gravitational and magnetic energies, energetic transductions to quantum magnetic and quantum electric energies are likely. Hydrogen is the most abundant element in the universe, so such ionization within stars results in plasma of mostly electrons and protons in rapid motions. These charges in motion generate huge magnetic fields for shift in behavior from Rule 3 to Rule 2 due to efficient energy transductions from C frame to L frames. So the great gravity of the stars holds the plasma together with fusion occurring internally to generate great thermal energy to sustain and energize the plasma, holding the plasma up against gravitational collapse (at least transiently by blend of Rules 2 and 3). The tremendous thermal energy within these structures is not simply random by Rule 3, the magnetic fields caused by the huge motions and interactions between ions, charges and spins of the plasma cause ordered motions and organized stellar structures for Rule 2 dynamics and effects also. Therefore on the basis of the Little Effect order exists in spite of such far from equilibrium conditions due to the fermionic spins and charges in rapid motions. Here it is demonstrated by the Little (Effect) Rules how systems far from equilibrium are not necessarily chaotic (Progigne, 1978) by Rule 3 but can manifest order by Rule 2 as the huge mass and gravity and consequent magnetism can organize even macro objects into Rule 2 behavior.

Magnetic fields associated with stars may be as much as a hundred trillion times the earth's magnetic field. The charges in rapid motions cause these huge stellar magnetic fields and the resulting magnetic fields order the internal motions within the plasma of stars by Rules 1 and 2. The tremendous magnetic fields in stars, neutron stars, pulsars and magnetars are a result of gravitationally compressed and densely, organized motions (revorbitals) of ions and electrons within the outer layers of these stellar bodies. The huge gravitational fields resist electric and magnetic repulsions between the like charges of the super currents and the huge thermal energies resist condensation of atoms in the outer shells. However deeper within the interior of these bodies, strong gravity may condense electrons, protons and neutrons into various exotic phases and by

assorted, magnetic, electric, weak and strong forces. It is further important to note that such gravitational forces become even greater within the deeper interior of these bodies such that tremendous densities approaching the nuclear range are the prevailing conditions (Wilhelmsson, 2002). Such extreme conditions cause the particles enough energy to obey a blend of Rules 2 and 3 as gravity is unified with other forces. Such blending of gravity to other forces and blending Rules 2 and 3 also exist on subatomic levels (even on earth) within atomic nuclei and electronic cores of heavy elements if but fleetingly and transiently. These great gravitational forces compress the neutrons, protons and electrons into various fluidic and solid phases even though the temperatures are millions of degrees by Rules 2 and 3. Such huge thermal, mechanical, electrical, magnetic and gravitational energies in stars allow efficient transductions not only to quantum electric and magnetic energies but transductions to nuclear energies involving sub-L frames with strong and weak forces. Such extreme motions, densities and interactions result in ordering of protons, neutrons and electrons. The fermionic ordering in shells, subshells, revorbitals and spin symmetries may be much different from that in terrestrial atoms for example nuclei and electrons may manifest magnetic valence and covalence by revorbital motions in these stellar systems relative to their valence in atoms on earth. On the basis of the Little Effect, the statistics and structures within the stellar cores are such that the quarks exist in pair revolutions (correlation) for spinrevorbital motions with the pairs revolving a third quark for a three body nucleon (triples) by blend of Rules 2 and 3. Furthermore protons, neutrons and electrons exhibit revolutionary (correlated) (spinrevorbital) motions for exotic phases, nuclei and compressed atoms and ions. The correlated revolutionary (spinrevorbital) motions of protons, electrons and neutrons lead to spin modulated fusion within the stellar cores on the basis of the Little Effect. For instance on the basis of the Little Effect with such nucleon correlated motions, it is thought that such antisymmetry, compressions and revolutionary (spinrevorbital) motions within the cores of neutron stars cause superconductivity of protons for extremely high temperature superconductivity (Itoh, 1969) by Rules 1-3. On the basis of the Little Effect, within the less dense outer stellar shells the magnetic ordering of the fermions by antisymmetry may also contribute to super currents and the resulting stellar magnetic field by Rules 1 and 2. In addition to the magnetic field organizing the supercurrents in these stellar bodies, on the basis of the Little (Effect) Rules the resulting magnetic fields may stimulate various physical phenomena occurring within these bodies by Rules 1 and 2. The magnetic fields from outer shell layers may organize fusion within the stellar core by Rules 1-3. The fusion within the core may drive the magnetism in the outer layers by Rules 1-3. The fusion processes within the core involve fermions, which

are governed by antisymmetry. It is currently thought that huge gravity and thermal energies within the core overcome antisymmetry for various fusion phenomena (Shopova, 2004) by blend of Rules 2 and 3. Here it is suggested on the basis of the Little Effect that the surrounding intense magnetic field from the shell currents can modulate the spins of electrons, protons and neutrons within the dense core and inner layers so as to flip spins for symmetry and boson states that allow fusion by Rules 1-3. On the basis of the Little Effect, here it is suggested that spin frustration of antisymmetry within the core drives fusion within the core and influence ion currents within the outer shells and the magnetic fields of the stellar bodies by Rules 2 and 3. The spin dynamics of fermions of the core are intimately coupled to the supercurrents and the consequent magnetic fields of the outer stellar layer by Rules 2 and 3 due to the huge mass and thermal, mechanical, electrical, gravitational, magnetic, quantum magnetic, and quantum electrical energies. On the basis of the Little (Effect) Rules, these spin interactions within the core are coupled with ion, electron, and proton motions in outer stellar shells so as to allow dynamic magnetic fluctuations that stimulate spin density within the stellar core for antisymmetry to symmetry phase transitions that allow fusion and modulation of fusion by blend of Rules 2 and 3. The blend of Rules 2 and 3 is due to the energy and mass densities (Rule 1) causing such huge magnetic fields from the core dynamics which are restricted in coupling magnetically to the surface currents by the large sizes of the stars, the limited speed of light, relativism of the ions in spinrevorbitals and the self-interactions of the spinrevorbitals such that the magnetic coupling is disrupted or broken between core motions and surface motions with the opening of the spinrevorbital motions and magnetic field lines from the cores to create gravitational fields and thermal energies at the surfaces. Under such conditions of blending Rules 2 and 3 over the whole (core and surface) gravitational and thermal energies are transformed to magnetic energies quantum magnetic, quantum electric and nuclear energies and vice versa. As fusion occurs rapidly, the magnetic field intensifies so as to cause antisymmetry within the stellar cores to slow the burning. As fusion slows, ion currents diminish to weaken magnetic fields allowing more spin density within the core and symmetry phases for fusion acceleration. Quite remarkably, the nontransient coupling and transduction of macromagnetic and macroelectric energies to quantum magnetic and quantum electric energies to nuclear energies (under strong and weak forces) whereby quantum magnetic orbitals break and reconnect in analog to dynamics of breaking and opening magnetic loops at the surfaces of the sun and stars.

The explanations of stellar events on the basis of the Little Effect are beautifully consistent with supernovas events and neutron star development and blackhole

development. Currently, these stages during the life of the star are understood on the basis of the masses of stars and their resulting gravities (Quiros, 2001) by Rule 3. Here it is suggested on the basis of the Little Effect that in addition to gravity, the more massive stars have faster and greater fusion rates with the resulting more rapid internal electron, proton, neutron and ion motions and therefore the magnetic fields are stronger in more massive stars by Rules 1 and 2. The higher temperatures, stronger gravity and stronger magnetic fields allow burning to heavier elements with the release of more energy by blend of Rules 1- 3. This exothermic fusion occurs up until the Fe nuclei are formed. Further fusion to heavier nuclei than Fe becomes endothermic. The elegance of this model by the Little Effect is not only does the thermodynamics of fusion beyond Fe by Rule 3 determine the ultimate destiny of the star, but also the unique strong spin exchange and polarizations that emerge with the Fe nuclei formation modify the kinetics of fusion by Rule 2.

Here it is suggested that the magnetic properties of Fe play a role in slowing the kinetics of fusion for such heavy and dense stars. Although some believe that the high temperature conditions result in complete ionization of Fe atoms under stellar conditions, it may be that the great gravitational and magnetic compressions by Rules 2 and 3 within the stellar core leads to some internal electronic structure in conjunction with the high core temperatures of the star by Rule 1-3. The antisymmetry of the electrons, neutrons and protons may lead to important magnetic phases and large magnetic and spin domains that are not as relevant in atoms of smaller atomic numbers as iron by Rules 1 and 2. Such novel magnetic phases, motions and structures of electrons about Fe nuclei can cause novel Fe magnetic valences for novel structures of Fe ions and magnetic bonding within and about Fe ions and atoms. This development of Fe during the stellar lifetime and the emerging magnetic properties may contribute to strong spin exchange and polarizations of the fermions that slow the fusion based on fermionic antisymmetry by Rules 1 and 2. For smaller core sizes, such antisymmetry is perturbed by coupling with surface currents by Rule 3 for sustaining core fusion. As the fusion processes increase to production of heavier (more magnetic) ions and phases toward Fe ions, the energy release and the coupling to the surface drive faster surface currents and the surface currents are polarized and perturbed by core spinrevorbitals of stronger magnetic moments of the stellar cores such that the surface currents reach limit of motions relativistically (and the size of the core to diameter of the star varies) for modulating the core antisymmetry to alter the modulation (to slow) of core fusion. Although in accord with the recent realizations on the basis of the Little Effect that lighter elements may exhibit ferromagnetism under proper conditions, the strongest exchange and spin polarization begin with Fe. With increase pressure and

temperature the domain regions of Fe increase in size by Rules 1 and 2. In principle, a fermion feels the magnetic torque of many atoms in the large spin phases and magnetic domains. It is as if the magnetism via exchange is a long range force just as gravity. Such mixing of Rules 2 and 3 and blending of magnetic and gravitational characteristics give a basis for unifying gravity and magnetism. On such basis the very high temperatures and pressures cause revorbital faster motions and greater magnetism and more mass of the dense energy with restrictions by $v < c$, limited speed of light, and the increasing size of the magnetic phase such that the correlation cannot self-interact so the magnetism forms gravity as Rule 2 goto Rule 3 over large space and long time in the stars as the self-interacting currents break and open and the magnetic field loops open to curved lines of gravity. Quite astoundingly this prior reasoning allows similar magnetic to gravitational transformations in cooler systems even terrestrial systems of smaller magnetic domains and magnetic field strengths over transient and very short times (hidden).

So as the star develops an iron cores the strong exchange and spin polarizations resist the external outer shell's magnetically induced spin density within the stellar core. Such magnetically induced spin density waves in the stellar core by the outer shell fields break the antisymmetry, which by breaking antisymmetry of protons and electrons allows further fusion within the core. The spin induced orbital effects on the fermions within the intense magnetic field from the outer shells cause the needed orbital transitions from free electrons to bound electrons to protons, which form neutrons. On the basis of the Little Effect, such spin induced orbital dynamics and spin density phenomena of the fermions of the stellar cores become modified as the cores become more ferromagnetic such that the spin density breaking of antisymmetry is slowed such that fusion cannot occur due to the electron, proton and neutron degeneracy as by Rules 1-3. On the basis of the Little Effect, this emergence of ferromagnetism with Fe accumulation causes a change in stellar fusion kinetics. This change in stellar fusion kinetics compliments the thermodynamics of nuclear binding energy as Fe accumulates to give greater explanation of supernova formation as by Rules 1-3. Therefore as Fe accumulates, fusion slows (due to the Little Effect) and the endothermicity of post-Fe fusion causes the star to suddenly lose its energy source such that it has nothing to oppose gravitational collapse by Rule 3.

The star therefore begins gravitational collapse by Rule 3. The increase in magnetic field within the core and the increase in density as the star collapse under gravity orient the fermions of the core such that fusion of electrons, protons and neutrons of the Fe core is not allowed based on degeneracy and antisymmetry by Rules 2 and 3. It is thought that during such collapse the bang of the outer stellar shell on its core causes a

supernova (Plewa et al., 2004) by Rules 1-3. On the basis of the Little Effect, here it is suggested that the bang causes cycles (based on elastic collisions of the shell with the dense core) of expansion and compression of the outer shells about the Fe core, which cause magnetic field ripples and oscillations in magnetic strength and directions by Rules 1-3. Here based on the Little Effect, it is suggested that more massive collapsing stars generate the stronger magnetic ripples and spin density waves within the stellar Fe core. These magnetic bangs break antisymmetry so that electrons and protons of the core may collapse to neutrons during the supernova such that a neutron star develops by Rules 1-3. The more massive stars create such intense magnetic ripples and compressions such that they may more thoroughly break antisymmetry and form blackholes by Rules 1-3. Therefore on the basis of the Little Effect, spin motions coupled to revorbital motions break the antisymmetry of Pauli degeneracy to allow fusion under gravity.

PYCONUCLEAR FUSION

The use of strong magnets may accelerate pycnonuclear fusion phenomena and contribute to greater reproducibility. Although a few papers have mentioned the use of magnetic field to accelerate lower temperature fusion no accepted mechanisms are given (Goyal et al., 2001; Sekershitskii, 1995; Heyl and Hernquist, 1996; Singh et al., 1992). Here the Little Effect provides a new mechanism whereby the magnetic field assists reverse beta. On the basis of the Little (Effect) Rules, pycnonuclear fusion phenomena are in general explained as spin induced revorbital effects that cause reverse beta processes. Such reverse beta eliminates the need for high temperature to overcome the Coulombic barrier. The observed conditions associated with sporadic and difficult reproduction of pyconuclear fusion events are supportive of this mechanism. These sporadic conditions are produced by laser irradiation, rf and microwave radiation and interfacial effects, nanosize particles and history of thermal stresses, electric stresses, pressure stresses, and mechanical stresses. Within these environments, the metal lattice absorbs large quantities of hydrogen. The absorbed hydrogen is likely ionized to p^+ and d^+ (Perrot, 1984). The p^+ and d^+ ions are coupled to the metal lattices by revorbital and spin interactions by Rule 1. The d^+ and p^+ ions are very strongly coupled to each other, metal ions and lattice electrons thru spin exchange. Pons and Fleischmann hypothesized a sort of fermionic to bosonic superradiance of the protium and deuterium within the lattice (Fleischmann et al., 1989). The Little (Effect) Rules govern the details of spin and revorbital phenomena associated with such superradiance. On the basis of the Little Effect, the discrepancy between the hot fusion ideology and new cooler fusion is resolved on the

basis of spin, revorbital and magnetics of the fermions for catalytic pathways to fusion phenomena that require lower temperatures. Here on the basis of the Little Effect, it is suggested that within the Pd lattice, the hydrogen atoms undergo oscillations between localized covalent bonds to Pd lattice and delocalized ionization for protium, deuterium and tritium ions within the lattice. On the basis of Little (Effect) Rules, these bond fluctuations determine a type of tautomerism. There are Coulombic and exchange interactions between the d^+ and p^+ and lattice electrons.

RB Little suggests that on the basis of the Little Effect that proton solvation (or electron solvation) of $(e_a^- \cdot p_a^+)$ spinrevorbital pairs (absorbed hydrogen atom) within the lattice causes spin induced electronic revorbital excitations by multi proton (or multi electron) interactions on the electrons (e_a) of the $(e_a^- \cdot p_a^+)$ pairs such that the intense motions of many surrounding protons (or electrons) and their associated spin exchange cause spin induced revorbital accelerations of the e_a into nuclear symmetry from the atomic symmetry of the 1s of the absorbed hydrogen, $(e_a^- \cdot p_a^+)$ by blend of Rules 2 and 3 on short times and small distances by hidden dynamics. The hydrogen atoms absorbed into a metal (like Pd) are subject to this because of the possible condensates of protons and deuterons within the Pd lattice's 5s, 5p and 4d revorbitals. The Pd affords a lattice with available 5s and 5p spinrevorbitals suitable for hydrogen ion condensations. Such 5s and 5p spinrevorbital symmetries allow the concentration of hydrogen ions and lattice electrons for internal hydrogen cluster solutes within the Pd lattice solvent. These lattice hydrogen clusters may have hydrogen surrounded by many protons or hydrogen surrounded by many electrons. Unlike the 4d of Pd, the Pd 5s and 5p spinrevorbitals manifest much stronger $(e_a^- \cdot p_a^+)$ spinrevorbital interactions with the Pd nucleus and much greater exchange interactions between $(e_a^- \cdot p_a^+)$ spinrevorbital pairs and exchange between the $(e_a^- \cdot p_a^+)$ spinrevorbital pairs and the lattice electrons and protons relative to such interactions within the Pd 4d spinrevorbitals. These greater Coulombic and exchange interactions cause the spin induced torque of the electrons of the pair into the protons to form neutrons by Rules 1-3. The phonons of the Pd lattice vibrate such protonic (or electronic) torque of the e_a into the p_a of the $(e_a^- \cdot p_a^+)$ spinrevorbital pair by Rules 1-3. Within such a lattice, s bands and p bands of Pd with the surrounding proton (or electron) spins and motions accelerate the electrons of the $(e_a^- \cdot p_a^+)$ spinrevorbital pairs into the protons. Likewise electrons around the $(e_a^- \cdot p_a^+)$ spinrevorbital pairs may by their motions and spin accelerate the electrons into the protons to form neutrons by Rules 1-3. These are complex multi-body interactions in magnetic fields approaching that of the neutron star at least on the length scale of the 5s spinrevorbital of a Pd atom and for very short times for hidden dynamics. It is

important to note that the magnetic flux density experienced by the hydrogen within the Pd lattice is huge on the scale of a Pd 5s revorbital. Exchange between atoms for small domains further intensifies such magnetic fields. Hydrogen clusters in such fields are stabilized (Buyvol-Kot et al., 2005). Such a lattice like Pd gives much greater stability to the hydrogenous clusters relative to the hydrogenous clusters in vacuum due to its electronic structure and electronegativity. Palladium's electronic structure allows the ready rehybridization of s,p and d revorbitals. As already considered, the electronic structure of Pd is such that the jj coupling applies (under ambient conditions) with the importance of both spin and revorbital momenta so that these momenta provide oscillating effects on the hydrogenous clusters for such spin accelerations of revorbital motions of electrons of the hydrogenous pairs into neutronic symmetry. In strong magnetic environments surrounding polarized electrons and protons can push on the bosonics diamagnetic $(e_a^- \cdot p_a^+)$ pairs to convert them to fermionic neutrons. On the basis of the Little Effect, such multi proton spin or multi electron spin interactions on e_a^- excites the pair into nucleon type spinrevorbitals on p_a^+ to a radius much less than the Bohr orbit so that the weak interaction may occur to create a neutrino and thereby cause the reverse beta process to convert the $(e_a^- \cdot p_a^+)$ spinrevorbital pair to a neutron by Rules 1-3. The neutron uptake by surrounding protons (or electrons) creates deuteriums. The neutron uptake by surrounding deuteriums creates tritiums. Tritium was detected in the magnet coil by SIMS. Excess levels of ^{18}O were detected in the cooling water of the DC magnet. Tritium decays to He-3. Thereby on the basis of the Pd lattice (or Cu-Ag lattice), spin induced revorbital dynamics of the lattice on $(e_a^- \cdot p_a^+)$ spinrevorbital pairs by surrounding proton condensates cause revorbital rehybridizations of electrons from atomic revorbital symmetry to nuclear revorbital symmetry in the form of an (electron-proton) or neutron particle by the spin induced revorbital accelerations of the electron in the highly concentrated polarized proton (or electron) rich media by Rules 1-3. The motions in the proton media begin to take on symmetry of proton motions in the nuclei which cause revorbital states of the electrons of the $(e_a^- \cdot p_a^+)$ spinrevorbital pairs to take on the electron motions as they exist within neutrons within the nuclei of atoms so that the electrons can undergo this catalyzed transition into the nuclear symmetry by Rules 1-3. This mechanism on the basis of the Little (Effect) Rules explains some findings such as the novel vortices and superfluidity in strongly interacting Fermi gas (Zwierlein et al., 2005).

This proton (or electron) media's spin induced fixation of the electron revorbital motions from the atomic symmetry to the nuclear symmetry is consistent with the handedness observed for the weak interaction during the beta process (Yan, 1979; Kouzakov, 2005). The handedness reflects the complementarity of weak and

electromagnetic interactions (Salam, 1979). On the basis of the Little Effect, just as the electrons accelerate in one direction in departing from polarized neutrons to form polarized protons (and electrons) in a strong magnetic environment, the strong magnetic environment reported here would organize proton (or electron) media so that the e_a would be catalytically accelerated in a suitable direction (Kouzakov, 2005) so that the specific handedness of the reverse beta process is met for a proton and electron to combine into a neutron. The rarity of reverse beta has to do with this selection rule. Neutrinos cause reverse beta in zero magnetic environment. On the basis of the Little Effect, magnetic interactions via spin induced acceleration of electrons in the proton (or electron) rich metal lattice allows such reverse beta with greater probability. This orbital motion of the electron tied to proton ($e_a^- \cdot p_a^+$) for neutron formation is stabilize under weak and Coulombic effects within the nucleus so the neutron is more stable within the nucleus within the fields and motions of internal protons. But extranuclear neutrons lack such proton field and motions so they rapidly undergo beta decay within 15 min. The rich proton (electron) environment in the Pd lattice allows such spin-orbital interactions with protons for the reverse beta to occur. These effects depend on magnetic properties of the media, which have been observed important for metals like Pd on the nanoscale (Burger, 1962). The magnetic and spin environment allow the torque of electrons from atomic electronic states to nuclear states. The existence of delocalized p^+ as fermions involves magnetic phases of the Pd lattice under prevailing conditions. Here it is suggested that the strong magnetic field may contribute to more reproducible pyconuclear fusion events as in the strong fields of neutron stars, pulsars and magnetars (Lugones, 2005).

In addition to the here predicted proton acceleration of electron into nuclear motion for ($e_a^- \cdot p_a^+$) spinrevorbital pair, here it is suggested that the Pd lattice can also by phonons torque the electron into tighter orbits so as to fuse the ($e_a^- \cdot p_a^+$) spinrevorbital pair into a neutron. This process may occur due to the alkali, alkaline earth like excited electronic states of Pd which can by four Pd^+ ions bind an ($e_a^- \cdot p_a^+$) spinrevorbital pair for a multi-centered 2 fermion bonds involving a bridging hydrogen or ($e_a^- \cdot p_a^+$) spinrevorbital pairs between 4 Pd^{46+} centers. The ($e_a^- \cdot p_a^+$) spinrevorbital pair may exist localized within the overlapping orbitals of four Pd centers. The motions of the Pd centers may accelerate electron and proton of the ($e_a^- \cdot p_a^+$) into tighter revorbital so as to form a neutron by Rules 1-3. The 4 Pd nuclei compress the ($e_a^- \cdot p_a^+$) spinrevorbital pair within their revorbital to form spinrevorbitals of ($e_a^- \cdot p_a^+$) pair just as atoms compress ($e_a^- \cdot e_b^-$) spinrevorbital pair into atomic and molecular orbitals in atoms and molecules by Rules 1-3. Such lattice phonons on the basis of the Little Effect cause revolutionary and correlation (spinrevorbital motions) of $e^- - e^-$ pairs for superconductivity. Likewise on the basis of

the Little Effect such lattice phonons cause correlation and revolutionary (spinrevorbital) motions of the ($e_a^- \cdot p_a^+$) pair that torque e_a^- into the p_a^+ for neutron formation. The Pd center experience huge Coulombic repulsion so they may not approach the ($e_a^- \cdot p_a^+$) spinrevorbital pair as closely as the previously described protons and electrons. But the slight approach would create huge forces due to greater nuclear charge on the Pd center.

In addition to this mechanism of reverse beta in the magnetic and spin environments of proton solvent and Pd multi-centers, here it is suggested on the basis of the Little Effect that the delocalized bosonic states wherein the hydrogen ions with an electron for ($e_a^- \cdot p_a^+$) exist in spinrevorbital motions by Rule 2 within the metal lattice may also contribute to important pathways to neutron formation. In magnetic environment, the ionized hydrogen exist as either fermionic p^+ and t^+ . But in low magnetic environments the hydrogen exists as pair bosonic spinrevorbital pair in revorbital motion within the Pd lattice just as an electron pair exists in revorbital motions within the lattice. Such ($e_a^- \cdot p_a^+$) bosonic spinrevorbital pairs may constitute a fusion mode in low external magnetic field environment by Rule 2. The ($e_a^- \cdot p_a^+$) bosonic spinrevorbital pair forms just as two electrons pair in revorbital motions such that the orbital revolutionary (spinrevorbital) motions in the partners spin field causes a countering magnetic force to their Coulombic interaction. In falling in accelerations, the particles of the pairs and triplets lose their Coulombic interactions to transduce to magnetic and gravitational interactions. By the Little (Effect) Rules, the spin of the proton of the ($e_a^- \cdot p_a^+$) spinrevorbital pair induces revorbital motions of the electron about the proton by Rule 2 so as to counter the Coulombic repulsive interactions between the p^+ and the Pd^{46} nucleus as the ($e_a^- \cdot p_a^+$) spinrevorbital pair approaches the Pd nuclei. The p^+ and Pd nuclei repulsion is lowered by the stronger bosonic pairing of ($e_a^- \cdot p_a^+$) in the Pd revorbitals about the Pd^{46+} nuclei. For the ($e_a^- \cdot p_a^+$) pairs, the electrons orbit the protons as they both move in the revorbitals of the Pd lattice for triples. The electron and proton ($e_a^- \cdot p_a^+$) pairs experience Coulombic attraction. The spinrevorbital motions of the electron about the proton cause its magnetic repulsion by the spin of the proton. But the electron spin and proton spin causes magnetic attraction. Within the s orbital of the Pd lattice the ($e_a^- \cdot p_a^+$) pair has a probability of approaching the Pd nucleus. On the basis of the Little Effect, such an approach by the Pd nucleus is energetically feasible if the electron orbits the proton very tightly causing greater relativistic effects. On the basis of the Little Effect, as the proton approaches the Pd nucleus the electron is relativistically accelerated into smaller orbits so as to counter the repulsion of the proton by the Pd nucleus by Rules 1-3. Not only does the local Coulombic field of the approaching Pd nucleus in its L frame twist the e^- into the proton, the surrounding many Pd^+ , e^- , and p^+ in the lattice (C frame) can form transient states of focusing the energy

into the $(e_a^- \cdot p_a^+)$ magnetic pair by Rule 2 for driving e^- into p^+ for neutron formation/stability and uptake of the resulting neutron by the Pd nucleus. The tighter electron orbit drives the electron into the proton to form a neutron under the force of the approaching Pd nucleus. This process provides a non-external magnetic (yet internal magnetism) route to reverse beta within the Pd lattice without external magnetic field.

On the basis of the Little Effect, it is also suggested that the $(e_a^- \cdot p_a^+)$ spinrevorbital pair may be relativistically driven into tighter orbits by its interaction and close approach to many lattice electrons. Such close approach would drive the e_a^- of the $(e_a^- \cdot p_a^+)$ spinrevorbital pair into the p_a^+ so as to lower its Coulombic repulsion by close nearby lattice electrons. So both the Pd nucleus and the lattice electrons may Coulombically force tighter orbits of $(e_a^- \cdot p_a^+)$ spinrevorbital for neutron formation. The possible high spin states of the nucleons of Pd nuclei can also contribute spin-orbital and spin-spin interactions between the Pd nucleus and the orbiting $(e_a^- \cdot p_a^+)$ bosonic spinrevorbital pair. Gamma rays and other photons may excite the Pd nucleus. The $(e_a^- \cdot p_a^+)$ spinrevorbital pair are perpetually exchanging virtual photons. On the basis of the Little Effect, the spinrevorbital motions of the absorbed $(e_a^- \cdot p_a^+)$ pair involve both stable discontinuum states as well as unstable continuum states by Rules 2 and 3. The electrons of the Pd lattice also undergo spinrevorbital motions to determine both stable quanta of discontinuum and unstable continuum states. On the basis of the continuum states of the $(e_a^- \cdot p_a^+)$ pair spinrevorbital and the continuum states of the Pd lattice electron pairs, an internal gamma oscillator can develop about stable discontinuum gamma quanta involving core Pd electrons. This gamma oscillator with inversion about discontinuum quanta states of the Pd lattice may cause lasing of gamma rays of sufficient energy to be adsorbed by the $(e_a^- \cdot p_a^+)$ spinrevorbital pair impurity. Here it is suggested on the basis of the Little Effect that these internal gamma lasing photons can simultaneously overwhelm virtual photons of the $(e_a^- \cdot p_a^+)$ spinrevorbital pair so as to excite the $(e_a^- \cdot p_a^+)$ spinrevorbital into tighter orbitals for weak exchange for neutron formation.

Such internal gamma lasing of possible discontinuum states and reversible exciting of intervening unstable continuum states with relaxations, excitations and transitions back to lasing discontinuum gamma states may explain the non-observations of gamma emission during LENR and other anomalous nuclear processes. It is important to relate the internal gamma inversion and lasing for metals for anomalous nuclear processes to internal phonon inversion and lasing in metals for photoelectric effect. Such internal gamma photons may be the basis of the so called burst observed in cold fusion phenomena. Magnetic phases may also cause internal triplet gamma lasing such that the gamma exchange between the Pd lattice electrons and the $(e_a^- \cdot p_a^+)$

spinrevorbital pair causes spin flip and change in multiplicity of the $(e_a^- \cdot p_a^+)$ spinrevorbital pair as it is driven into the neutron symmetry. The spin field of the proton and possibly the Pd nucleus and the electron orbit in this spin field cause spin induced orbital acceleration of the electron about tighter orbit about the proton. The relativistically tighter the orbit of the $(e_a^- \cdot p_a^+)$ pair appears as a neutron to the Pd nucleus. It is important to note the great magnetic force on these subatomic length scales. So on the basis of the Little Effect, the trio of electron, proton and Pd nucleus (triples) develop a state within the s revorbital of the Pd such that the $(e_a^- \cdot p_a^+)$ spinrevorbital pair forms a neutron due to motion within the Pd lattice involving close approach to Pd nuclei. The closer approach of the $(e_a^- \cdot p_a^+)$ spinrevorbital pair to the Pd nucleus drives the reverse beta formation of a neutron. The gamma exchange between the electron of the $(e_a^- \cdot p_a^+)$ spinrevorbital pair and Pd nucleus prevents gamma between the $(e_a^- \cdot p_a^+)$ so electron barrels into the proton of the pair for weak interaction to form neutron. Therefore here it is proposed that an internal laser of gamma frequency develops in the Pd lattice such that coherent gamma photons overwhelm the $(e_a^- \cdot p_a^+)$ spinrevorbital pair into weak interaction to form neutrons. It is important to note that within the nucleus gamma exchange keeps the beta process from occurring. This model explains recent fusion of deuterium within erbium deuteride lattice. They observed fusion by firing d^+ into ErD_2 . On the basis of the model and application of Little (Effect) Rules, the neutron star and pulsar magnetar are put forth as further evidence for model such that the huge magnetic fields in these celestial bodies may accelerate reverse beta events (Goyal et al., 2001, Singh, 1992). In time stronger evidence mounts for pycnonuclear events in metal lattices even if currently at impractical rates (Naranjo et al., 2005; Szpak et al., 2005; Osman et al., 2005). Also the magnetic field, pressure and temperature conditions in the Fe core of the earth may contribute to cold fusion effects within the earth. Some evidence of geo-cold fusion has been put forth on the basis of He-3 tritium in lava of volcanoes (Jones and Ellsworth, 2003).

Conflict of Interest

The author has not declared any conflict of interest.

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Full Length Research Paper

Characterization of porcelain tableware formulation containing bentonite clay

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Aluminosilicate are often produced from kaolin with a kaolin bond in the formulation intended to increase the thermal strength of the product. Because kaolin formulations do not sinter well, investigation of methods for increasing the density of kaolin is highly relevant. The density can be increased by increasing the degree of dispersion. An additive which improves sinterability would be especially effective. Bentonite with its high plasticity and reactive surface meets these requirements to a certain extent. Four formulations of the porcelain tableware were prepared in different percentage from 0 to 15 wt.% of calcic bentonite. The mass loss and shrinkage of different formulations were measured by using the following thermal analysis such as: Differential thermal analysis (DTA), thermal gravimetric analysis (TGA) and dilatometric analysis. Its density, water absorption, total porosity and the flexural strength were also measured at different temperatures between 1250 and 1400°C. It was found that the bentonite added to the formulation increases the strength of the product and reduces the total porosity to 3.35% by increasing the degree of dispersion during the grinding of the components, thereby improving the sintering process of the formulation. On one hand, the weight loss, shrinkage and sintering time were decreased. On the other hand, the thermal resistance and flexural strength were increased at 1380°C for 10 wt.% of bentonite content.

Key words: Firing, suspensions, total porosity, thermal properties, flexural strength, bentonite.

INTRODUCTION

Formulations of traditional porcelain usually involve 25 wt.% of plastic component, 25 wt.% silica and 50 wt.% feldspar (generally sodium feldspar) for soft porcelain and 50 wt.% of clay, 25 wt.% silica and 25 wt.% feldspar (generally potassium feldspar) for hard porcelain

(Jouene, 2001; Alessandro, 2007). Bentonite is a natural mixture of minerals, it is characterized by a high capacity adsorption, ion exchange and swelling. There are two types of bentonite: sodic and calcic. In order to realize the sodium bentonites, the calcic bentonites are treated by

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sodium hydroxide because they have the highest capacity of swelling. Bentonite is used extensively in various branches of industry such as paper, food, pharmaceutical and petrochemical industries, etc. (Savic et al., 2014a). Also, bentonite has been applied in environmental preservation when removing heavy metal ions from wastewater (Savic et al., 2012; Savic et al., 2014b).

The obtained results by Rodriguez and Torrecillas (2002); García and Aguilar-Elguézaba (2009); Andreola and Siligardi (2009) of the use of the bentonite in the different formulations of ceramic pastes for wall tiles, bricks, ceramic tiles and porcelain stoneware are:

- (1) Processes during firing are different from those of the classical formulation of kaolin.
- (2) Better control of the dimensional characteristics of pieces during firing has been achieved.
- (3) Technological parameters pieces formulated with bentonite (shrinkage, modulus of rupture, apparent density, water absorption, expansion by humidity) satisfy the industrial requirements for the production of wall tiles and they have an important function: to confer plasticity in the green state and, during firing, undergo some structural modifications which furnish the main oxides to form some important phases such as mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$).

Substitution of clay by the bentonite treated thermally present economic advantages, increases the strength of the product and reduces the total porosity. The obtained porcelain tiles mixtures represent the plastic components that affect the rheological behavior, that is, it increases the viscosity and thixotropy. The elasticity and resistance to rupture were increased by using the bentonite in the ceramic formulations with 10 wt.%.

The held exchangeable cations on the layers' surface were linked together. The intensity of these bonds depends on the valence of the cations (Wakim, 2005). The more compensating cations are small and weakly charged, the more the clay swelling is important. Therefore, in this study, the bentonite swelling is low because the exchangeable cations are Ca^{+2} . As a result, the specific surface is low. The reactive surface of bentonites takes the form of lateral faulted bonds and external basal-plane boundaries with a very low negative charge. For minerals of the kaolinite group the reactive surface is represented only by the edge regions of the crystals at the rupture sites on the bonds Si-O-Si and $\text{OH-Al}^{\text{IV}}\text{-OH}$ when the fringe atoms of oxygen or hydroxyl are incompletely sutured with silicon and aluminum respectively.

The aim of this paper provides the performance of the nature of interactions between raw materials and calcic bentonite for producing the material porcelain tableware. According to the previous studies, the resulted materials using the calcic bentonite are not enameled. The obtained formulations are characterized in terms of: physical, mechanical and thermal analysis.

EXPERIMENTAL METHODS

Location of raw materials

The different formulations of porcelain tableware (0, 5, 10 and 15 wt.% of bentonite) were composed of kaolin from Djebel Debbagh, Guelma (Algeria) used in formulations tableware. The quartz comes from the Boussaâda area, the Feldspar from the Bouira area all in Algeria; and the bentonite was calcined in a continuous roller kiln (heating to 973°K with a heating rate of 5°Ks^{-1} and maintained at this temperature for 3m). To this is added a sodium tripoliphosphate ($\text{Na}_2\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$) as deflocculant (0.3 wt.%) to improve the dispersion of the slurries.

Raw materials characterization

Mineralogical analyses were carried out with a diffractometer (Philips PW 1710, France) in step scan mode using Ni-filtered CuK α radiation (1.5406 Å); wide-angle X-ray spectra were recorded with a D 500. Elementary chemical analyses were performed by ICP (Induced Coupled Plasma) references Iris, marketed by Thermo Jorrell (Cheshire, England).

Samples preparation

The standard composition of triaxial porcelain, defined as P₀ (0 wt.% of bentonite), was the formulation reference. Three formulations, with increasing amounts of bentonite (with respect to P₀), designated from P₁ to P₃ (the number refers to the wt.% of bentonite in the batch), were produced in laboratory conditions via pouring and sintering. Table 1 summarizes the batch formulations and the chemical compositions of the porcelains (in wt.%). Bentonite was used in the three batches replacing feldspar that is normally used in traditional compositions. The main observations show the role of the bentonite as a fluxing agent.

Various formulations were dry-milled in a ball mill for 4 h and subsequently wet-milled in a ball mill for 40 m. In general the size of quartz and feldspar reached a value of (45 and 53 μm) respectively, to increase the strength and verification of porcelain material (Bragança and Bergmann, 2004). The resulting slurries were passed through a 63 μm sieve to calculate the residue on sieve. Values were between 5 and 7% depending on production requirements (Rodríguez and Torrecillas, 2002). The mixtures sunk in plaster rectangular molds were dried at room temperature for 48 h and at 105°C for 24 h. The samples were fritted at the temperatures of: 1250, 1300, 1380 and 1400°C (heating and cooling rates $5^\circ/\text{min}$ and 1 h soaking at the highest temperature). The starting temperatures were chosen based on the respective liquidus temperatures of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$ systems.

Characterization of samples

Differential thermal analysis (DTA, Netzsch, STA 409) and thermal gravimetric analysis (TGA, Netzsch, STA 409) were carried out using standard procedure with alumina as reference, the analysis results of dilatometric analysis were measured in the apparatus (NETZSCH, 402C heating rate $5^\circ\text{C}/\text{min}$). The flexural strength was performed using equipment of a mark (Zwick / Roell) (Reference Z2.5KN), 0.5 mm/min displacement.

To characterize the fired specimens, water absorption was measured according to the ISO-standard 10545-3, 1995; weight gain of dried bulk samples after immersion into boiling water for 2 h, cooling for 3 h and sweeping of their surfaces with a wet towel.

Table 1. Formulations (in wt.%) of the model porcelain P₀, P₁, P₂ and P₃.

Raw materials	Mass percentages (wt.%)			
	P ₀	P ₁	P ₂	P ₃
Kaolin	55	55	55	55
Feldspar	25	20	15	10
Quartz	20	20	20	20
Bentonite	0	5	10	15

Table 2. Chemical composition of raw materials (wt.%).

Materials	Oxides (wt.%)								
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	K ₂ O	Na ₂ O	CaO	MgO	MnO
Kaolin	45.30	39.13	0.41	0.07	0.21	0.04	0.15	0.05	0.02
Quartz	95.33	1.35	0.12	0.41	0.45	0.04	0.94	0.13	/
Feldspar	77.01	12.03	0.145	1.13	5.68	2.06	0.28	0.29	0.042
Bentonite	65.2	17.25	0.2	2.10	0.2	2.15	3.10	1.20	/

True density (D_T) was determined by the densimeter Candlot- Le Chatelier and apparent density (D_A) by Archimedes method. The total porosity (P %) was then calculated using Equation (1). 80 parallelepiped bars (3 × 4 × 40 mm) were used for flexural tests (three point bending)

$$P (\%) = (D_T - D_A / D_T) \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Raw materials and porcelain formulations

XRD analyses were carried out to determine the mineralogical compositions. The results show in the kaolin the presence of kaolinite ($Al_2Si_2O_5(OH)_4$) as the main phase and halloysite ($Si_2Al_2O_5(OH)_4 \cdot nH_2O$) as a secondary phase. Feldspar is composed of feldspar potassic ($KAlSi_3O_8$) and anorthite ($Si_2O_8CaAl_2$). Quartz is composed of quartz (SiO_2) and traces of Ca, Mg and Al. The bentonite spectra indicate the presence of quartz, feldspar, cristobalite and carbonate (calcite) and it has a high proportion of montmorillonite.

Table 2 shows the chemical analyses of the raw materials. These results deduced from the elementary chemical measures analysis by ICP, showed that the kaolin contains small amounts of impurities such as Fe_2O_3 , K_2O , CaO and MnO ; this is consistent with the white clay kaolin. The proportion of SiO_2 in the feldspar more than 50 wt.% can contribute the formation of the liquid phase. The percentage of SiO_2 in the quartz from Boussaâda exceeds 80 wt.% according to García and Aguilar-Elguézaba (2009) and the results obtained of raw materials used are alumino-silicate materials. Besides, it is important to note the iron oxide content of the samples

for their use into porcelain tableware: the bentonites having a $Fe_2O_3 > 5\%$ will not be used to avoid the black core and changes on colorimetric properties of the ceramic porcelain after firing. The bentonite contains $Fe_2O_3 < 5\%$ and more MgO and slightly less Al_2O_3 compared to other raw materials.

Vitrification behavior

TGA and DTA of the four porcelain samples are shown in Figures 1 to 4. Major endothermic peaks at 122, 111.4, 122.1 and 113.1°C for 0, 5, 10 and 15 wt.% bentonite, respectively, were attributed to the elimination of water of clay minerals. Mass loss associated with these peaks was about 13.88, 13.36, 12.22 and 13.78% for 0, 5, 10 and 15 wt.% bentonite, respectively. Endothermic peaks at 526.1, 519.3, 538.1 and 515.1°C for 0, 5, 10 and 15 wt.% bentonite, respectively, were assigned to the dehydroxylation of the hydroxyl groups in the kaolin to form metakaolin ($Al_2O_3 \cdot 2SiO_2$) (Schneider et al., 1994) and dehydroxylation of montmorillonite (Celik, 2010). Mass loss associated with these peaks was 3.78, 3.67, 3.70 and 3.58% for 0, 5, 10 and 15 wt.% bentonite, respectively. Knowing that the bentonite stores some amount of water between its layers (Alessandro, 2007; García and Aguilar-Elguézaba, 2009), high quantity of water evaporated after a heat treatment of porcelains mixtures P₁, P₂ and P₃.

Exothermic peaks appeared at 1004.70, 1003.70, 996.70 and 1008.61°C for 0, 5, 10 and 15 wt.% bentonite, respectively. Mass losses associated with these peaks were about 1.10, 0.87, 0.77 and 0.81% for 0, 5, 10 and 15 wt.% bentonite, respectively. The bentonite added to

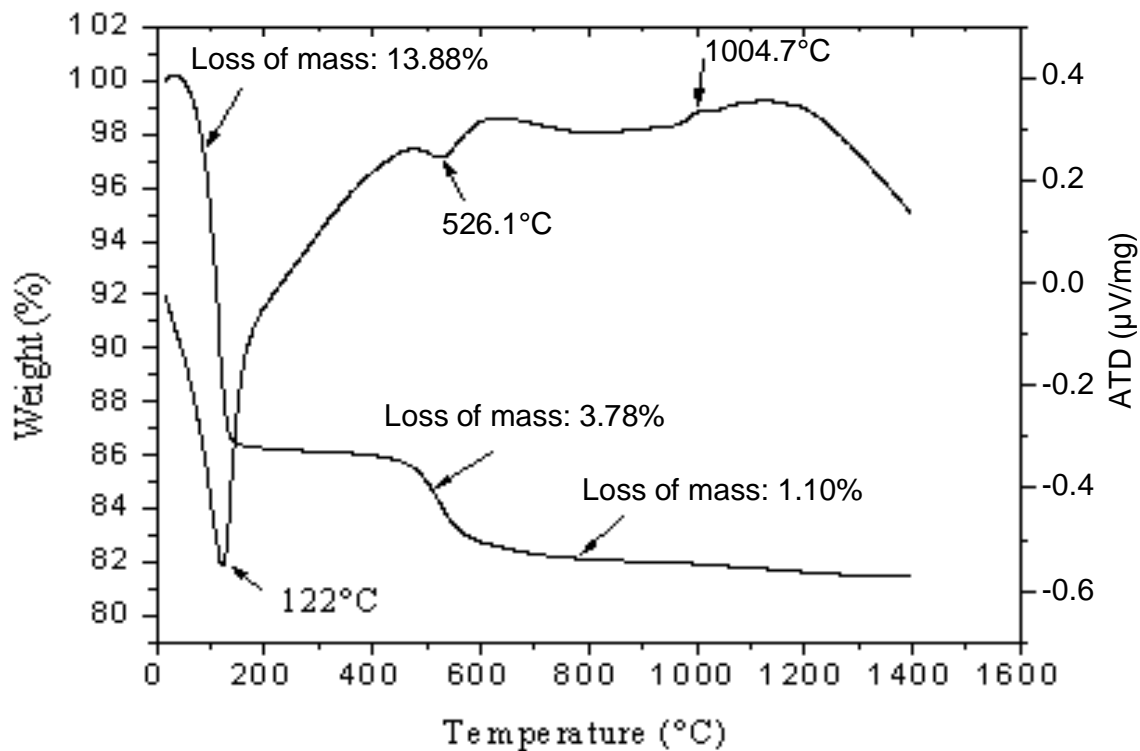


Figure 1. ATD/ATG analysis of the mixture, with 0% of bentonite.

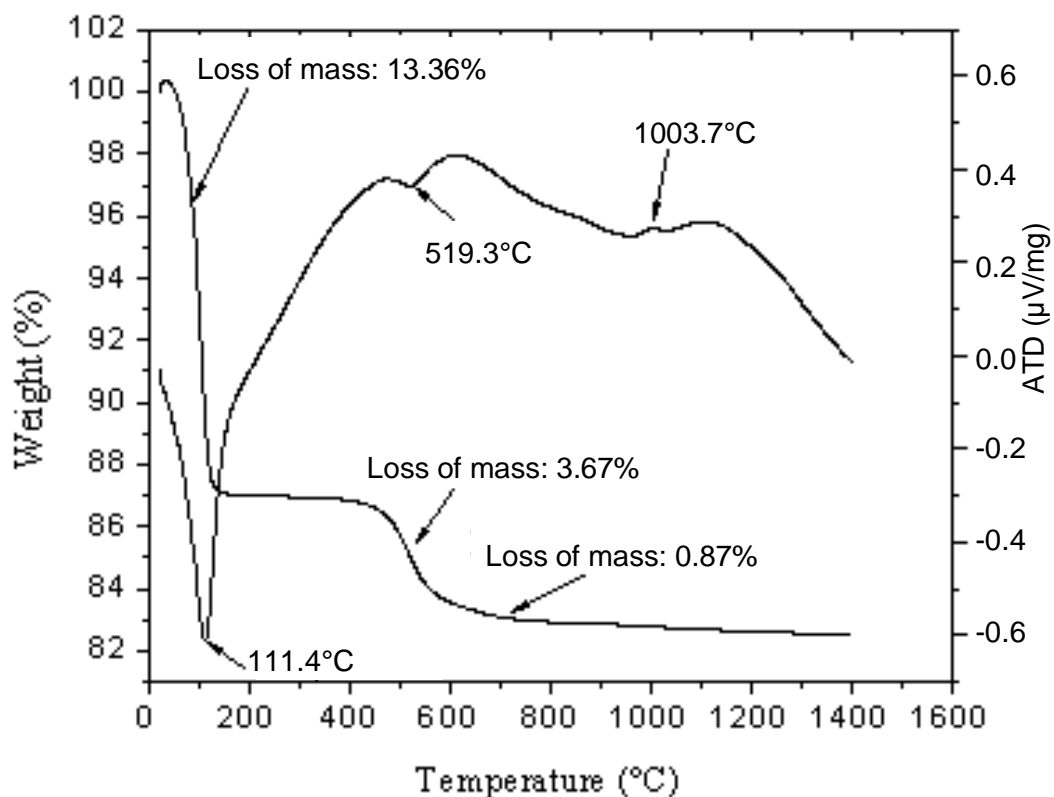


Figure 2. ATD/ATG analysis of the mixture, with 5% of bentonite.

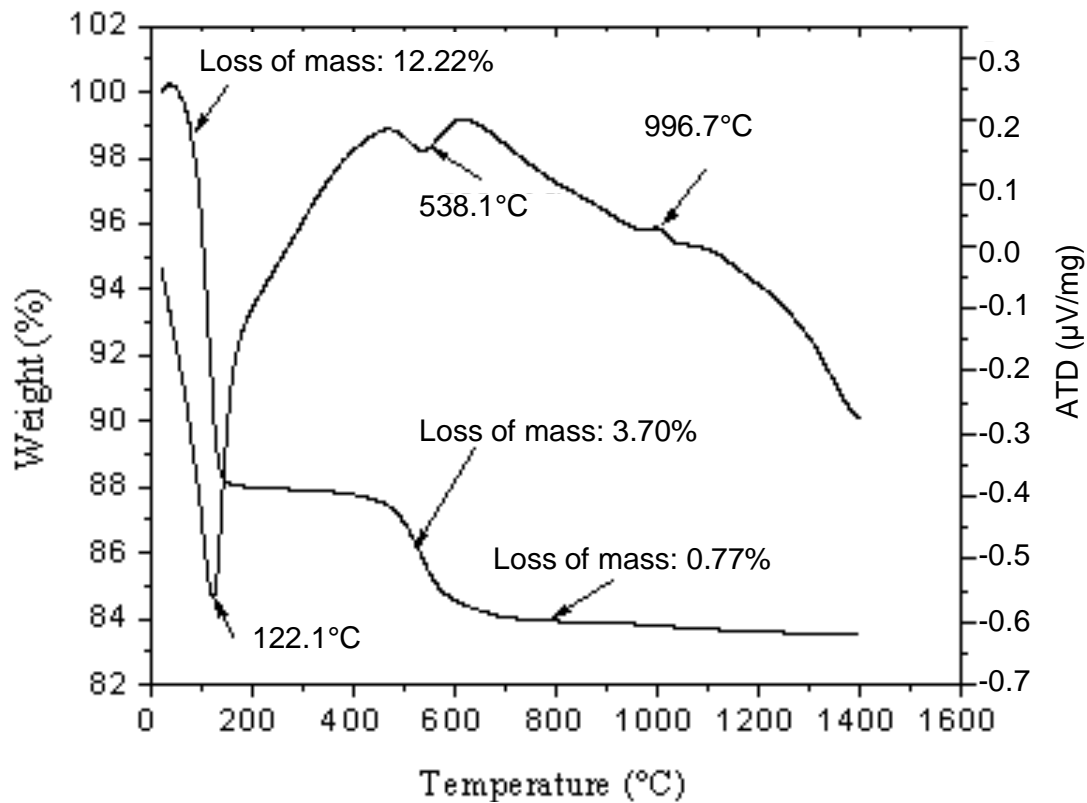


Figure 3. ATD/ATG analysis of the mixture, with 10% of bentonite.

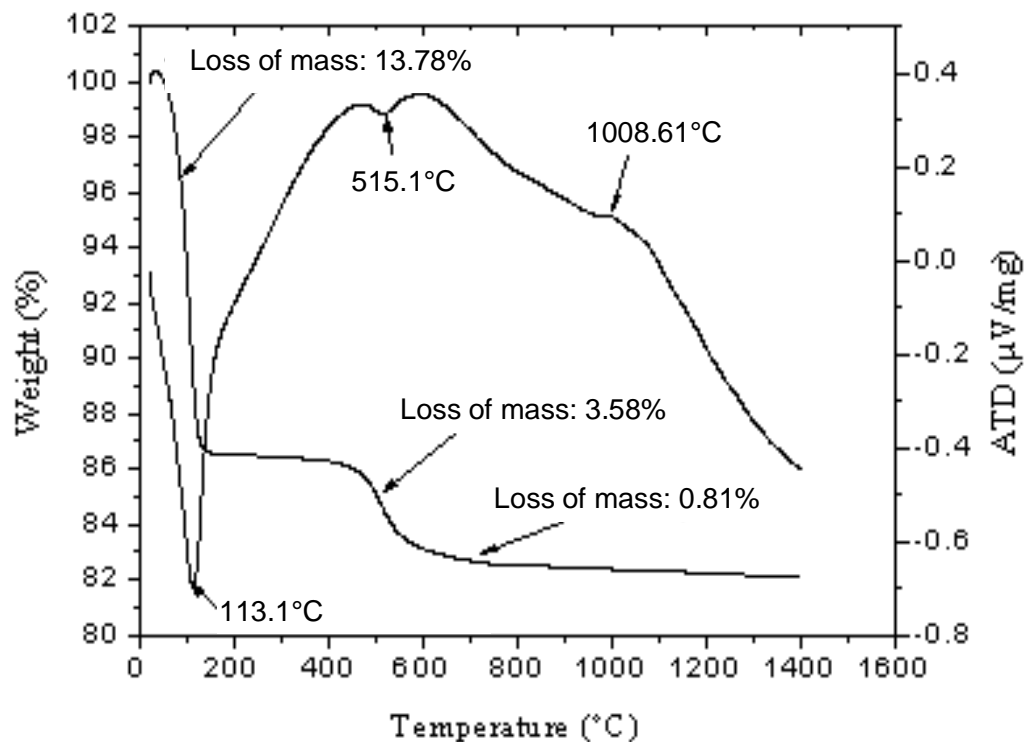


Figure 4. ATD/ATG analysis of the mixture, with 15% of bentonite.

the formulation increases the strength of the product by increasing the degree of dispersion during the grinding of the components, improving the sintering process of the formulation (the firing temperature of the formulations 0, 5, 10 wt.% of bentonite was: 1250, 1300, 1380°C. For the formulation 15 wt.% of bentonite was undetermined).

The TDA analysis showed a considerable liquid phase was formed, that has contributed to the fusion of bentonite (García and Aguilar-Elguézaba, 2009). It is considered that these changes are consistent with a mechanism of liquid phase sintering. This mechanism concerns the dissolution of the solids in the liquid phase and growth in the crystalline phases demonstrated by (Kingery et al., 1976; Celik, 2010). The closed pores are generated by the gas trapped and micro pores are generated by the process of crystallization (Karamanov and Ferrari, 2006). The ATG experimental analysis showed that the total mass loss mixtures of 0, 5, 10 and 15 wt.% of bentonite were: 18.76, 17.90, 16.69 and 18.17% respectively, and the lower value correspond to the mixture of 10 wt.% of bentonite.

After the high temperature treatment of bentonite, these polycationic species are transformed after dehydration and dehydroxylation into rigid pillars, linked permanently to the silicate layers. This process "pillar" leads to the formation of two-dimensional micro and/or mesoporous materials, known as pillared clays which are characterized by a good thermal stability. The thermal analysis results showed that the choice of raw materials percentages and development processes in thermal treatments should be imposed to a weight of 10 wt.% in bentonite.

Values of maximum density, water absorption, total porosity and flexural strength of formulations for 0, 5, 10 and 15 wt.% of bentonite are: (2.48, 2.55, 2.59 and 2.68 g/cm³), (0.16, 0.09, 0.03 and 0.56%), (5.42, 3.72, 3.35 and 6.23%) and (90.71, 120.88, 135.07, and 36.43 N/mm² and represented in Figure 5. The density for the porcelain of 10 wt.% bentonite was 2.59 g/cm³ at 1380°C, at this temperature, porcelain had water absorption value of 0.03% and total porosity of 3.35%.

Water absorption and porosity reduces with increasing firing temperature. This is due to the increasing formation of glass phase. The liquid phase aids in sintering, thereby increasing consolidation at higher temperatures. The firing temperature that gave maximum strength was approximately the lowest value of water absorption. It may be noted that maximum strength and maximum density were obtained from the same firing temperature. The highest flexural strength (that corresponds to the highest optimal density) was 135.07 N/mm² for 10 wt.% of bentonite (which corresponds to the firing temperature 1380°C). For percentages (0, 5 and 15 wt.% of bentonite) the flexural strength was: 90.71 (1250°C), 120.88 (1300°C) and 36.43 N/mm² (1400°C), respectively. Density is a property that has a strong influence on the mechanical strength. In general, the higher the density, more strength

increases. The increased amount of liquid phase at higher temperature certainly affects negatively the mechanical strength. Generally, in ceramic compositions containing clays and feldspars, increased temperatures result in higher mullite formation, thereby improving mechanical properties.

Many studies have described the influence of the sum Fe₂O₃ + TiO₂ from which the chemical composition is rich in the bentonite and favors the process of sintering of the ceramic matrix and the formation of a mullite composition of 10 wt.% bentonite (Kausik and Kumar, 2004; Kamseu et al., 2007; Andreola and Siligardi, 2009). Ti⁴⁺ and Fe³⁺ play important role by either substituting Al³⁺ or by their integration into the structural interstices of the matrix.

Increasing the amount of bentonite increases the formation of more of the liquid phase, density, the flexural strength; and decreases the porosity and water absorption. The dimensional changes observed after firing of the mixtures of porcelain P₀, P₁, P₂ and P₃ are given in Figure 6. Slight shrinkage surroundings between 33.62 and 112°C for percentages 0, 5, 10 and 15 wt.% of bentonite is due to the elimination of water of clay minerals. The maximum expansion rate between 112 and 600°C was 593.75°C; its percentage corresponds to 15 wt.% of bentonite. There was a small expansion of percentage mixtures 0, 5, 10 and 15 wt.% of bentonite between 500 and 600°C due to the α→β-quartz transformation (Celik, 2010). An initial shrinkage started at around 542.42, 555.75, 542.42 and 593.73°C of percentages 0, 5, 10 and 15 wt.% of bentonite respectively, due to the formation of metakaolinite. A second shrinkage from 808.30, 814.08, 865.97 and 804.84°C was attributed to sintering and formation of vitreous phases (Celik, 2010).

The maximum shrinkage rate between 990.22 and 1400°C was obtained at 998.59°C for the composition 15 wt.% bentonite. When the temperature reached 1034.20°C, the rate of shrinkage was approximately low - 1.24% that corresponds to the composition of 10 wt.% of bentonite between the high temperature and room temperature. In particular the last step between 990 and 1400°C is an advantage in the use of bentonite. In the industrial process, the dimensional change should be minimal (García and Aguilar-Elguézaba, 2009; Dondi et al., 2014). The smallest shrinkage was due to the percentage 10 wt.% of bentonite.

Conclusion

Based on the results of the present study, the following conclusions can be drawn: the incorporation of small quantities of bentonite in raw materials represents a great potential in industrial porcelain. The bentonite occupies an important role in the mechanism of various steps of fire. The influence of bentonite increases the thermal resistance, densification and improves thermal firing

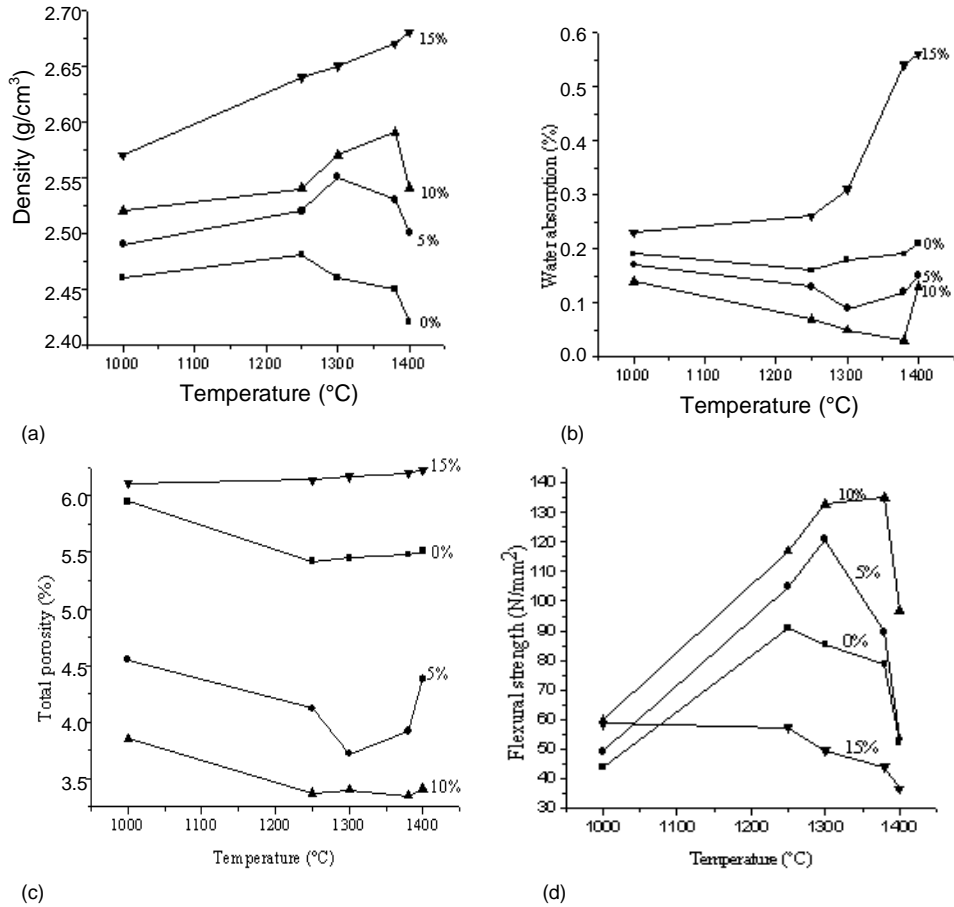


Figure 5. Influence of sintering temperature on mixtures 0, 5, 10 and 15 wt % of bentonite: (a) Density, (b) Water Absorption, (c) Total porosity, (d) flexural strength.

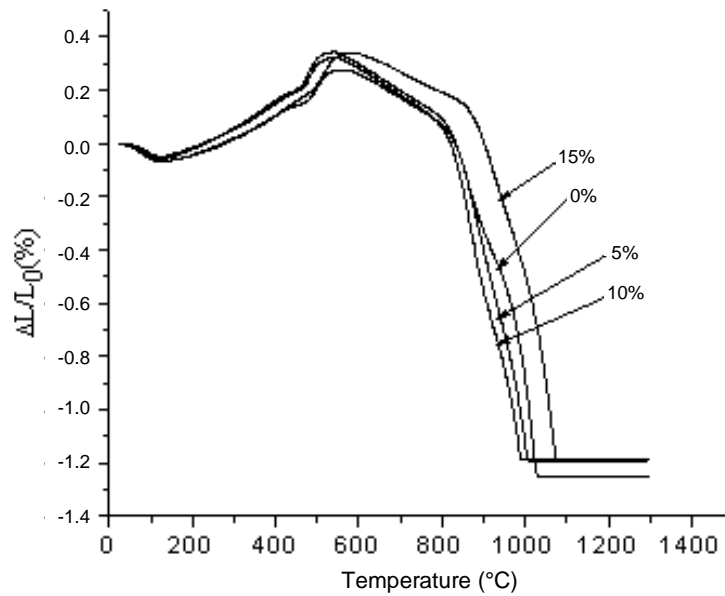


Figure 6. Shrinkage behaviour of porcelain tableware made of the formulations 0, 5, 10 and 15wt % of bentonite.

cycle of the porcelain tableware. Densification was perfect and the firing cycle was short compared to the porcelain without bentonite. The appropriate percentage of bentonite is 10 wt.%.

Conflict of Interest

The authors have not declared any conflict of interest.

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Full Length Research Paper

Correlation between milling time, particle size for stabilizing rheological parameters of clay suspensions in ceramic tiles manufacture

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Several parameters governed the rheological properties as well as the nature of the constituents, to the process of implementation. One of the major solution is to master the milling time which is responsible for the fineness of the grains, which in turn, conditioned the correct handling of the sintering mechanism, and allows highlight of the correlation between the size of the powders and the rheological properties. The introduction of a powder in a liquid induces changes in the interface of the solid phase when it passes from the vapor phase, to the liquid phase. To improve this understanding, we studied the influence of these parameters on the good dispersion of particles and more particularly the grain size. To do this, four mixtures composed of clay, kaolin, feldspar and sand were considered. The difference between each mixture, is the substitution of kaolin by feldspar with a decreased of kaolin (8%) compared to the initial rate. Each mixture was to undergo three grinding duration (-1 h, 30 min, 1 h and 2 h). The analysis of the rheological properties allowed us to note that the best flow was obtained with mixtures C3, C4, C5, corresponding to a grinding duration of 1 h 30 min. We also observed a clear correlation between the grinding time and viscosity. After drying of the suspensions, the powders obtained are grounded according to three types of particle sizes (0.25 - 1 and 1.25 mm) then pressed in the form of ceramic tiles physical-mechanical, analyses were performed on the cooked products. After optimization and comparative study between the different mixtures, it was found that the M3 mixture, with grain size of 1.25 mm provides the best products. The measured values are in agreement with the requirements of manufacturing standards and offer a higher mechanical strength to the tiles manufactured industrially.

Key words: Grinding, powder, stability, rheological parameters, ceramic tiles.

INTRODUCTION

In order to give impart to the ceramic powder of the rheological properties desired and cohesion during the

step of shaping it becomes necessary to control the choice of a number of parameters to be used which

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Table 1. Chemical analysis raw materials

Elements	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	Loss ignition
Clay	49.09	15.05	6.09	10.10	1.93	0.15	1.93	0.66	0.15	0.74	14.09
Kaolin	69.12	15.65	2.38	1.23	0.26	0.01	5.47	2.02	0.22	0.24	3.39
Feldspar	70.54	17.54	1.50	0.25	0.36	0.01	3.76	0.37	0.06	0.32	5.29
Sand	95.65	0.68	0.29	1.36	0.08	0.01	0.22	0.02	0.01	0.07	1.61

include: The granulometric properties and morphological state agglomeration. The physical characteristics of a powder are the agglomeration phase, shape, particle size, density and specific mass (Bertrand and Edward, 1995). Granulometry ceramic particles can vary depending on the purpose of products.

The average size of the final particles depends on the used technique, the characteristics of the grinding body (material, shape, size), the milling time, and the medium (dry grinding, in an aqueous or non-aqueous medium, with or without dispersant and charge ratio). The disintegration and dispersion of the ceramic particles are fundamental steps in the methods of shaping by way, liquid, plastic or dry. A good dispersion technique allows minimizing the final quantity of defects in the uncooked body and the final ceramic pieces.

The rheological properties of the suspensions are very sensitive to the particle size distribution and their specific surface. The minimum viscosity can be reached if a mixture contains a fine/coarse ratio 36/64. The adaptation of the physical characteristics is mainly performed by grinding, granulating and selection (Boch, 2001). The wet grinding may have some advantages over dry grinding, although, wear of the balls can be much higher for the same material and requires 30% less energy than dry grinding for size reduction equivalent (Hausonne et al., 2005)

EXPERIMENTAL PROCEDURE

The study is carried on the use of the following raw materials: clay, kaolin, feldspar and sand. The elementary chemical analyses were carried out in an X-ray fluorescence spectrometer type PW2540 Vrc Change Sample Dy-1189. The mineralogical analyses were carried out in diffractometer X 'Pert PRO, Dy-type 2233-0525. Granulometric analysis was performed by pipette "Robinson". The mechanical strength was determined with a bending device Gabrielli type - Model: 424 CRAB. The used process is wet way process. Raw materials (plastic not plastic) were ground in a wet medium with humidity of 40% in earthenware jars "Gerhards," type TPR, with grinding body in alumina beads and with grinding times of up to 1 h 30 min and 2 h. The resulting powders was humidified at 7 and 8%, and then sieved, with a mesh opening (0.25 - 1 mm and 1.25 mm) sieve. Sieving of the powders were obtained after drying the slurry made in a sieve Haver & Becker type. The pressing is done using a hydraulic press semi-automatic Gabrielli 262367 type. Drying the ceramic tiles is done in a laboratory oven Memmert type with a temperature of 110°C. The raw shard cooking is performed in a rapid-firing oven model: N200A, type NR: 55269 with a temperature of 1180°C within 50 min.

RESULTS AND DISCUSSION

Chemical analysis

Chemical analysis of raw materials is listed in Table 1. The predominant elements in the clay, kaolin and feldspar are SiO₂, Al₂O₃, K₂O and CaO. In the clay case, the rate of CaO is in the range of 6 to 20%, the clay is "marly". The mass ratio of Al₂O₃ to Fe₂O₃ of all considered materials is equal to 5; this will give a broken pink because it is between 3 and 5%. The deformation and removal should be taken into consideration because of the low refractory nature of raw materials (Boch, 2001).

A high concentration of SiO₂ means that it is present in the raw material which is in two forms. The origin of the silica is in the mantle, zone of the heat convection and zone transformation of the substances. It is located in the peripheral areas of granites (pegmatites, for example), in hydrothermal lodes, in metamorphic and sedimentary rocks. The Al₂O₃ is present under low content 45%. This allows the deduce of clay and kaolin with both having a low refractory nature, and low plasticity.

The Fe₂O₃ is much more present in the clay which gives it the properties of clay which is slightly ferruginous. The iron acts as a melting element during firing by forming eutectic melting at lower temperatures. CaO, whose presence indicates that the mineral contains plagioclase and comes from the carbonates. It acts as a melting element, and combines it with the silicates during cooking.

The Na₂O, K₂O, are alkaline oxides, which comes mainly from feldspars, illites, micas and smectites. They play the role of fondants and also act as melting. Their associations with iron oxide, occurs during firing the sinterizing reactions, which gives the products, their definitive qualities.

TiO₂ is an accessory mineral present in many metamorphic rocks (gneiss, mica schist, granulite, eclogite, etc.) in magmatic rocks (granites, syenites, etc.) in pegmatites and quartz lodes. In alluvial sands, it is much more responsible for the yellow color (Tarassoff et al., 2006). The high value loss on ignition of clay comes from the release of CO₂ due to carbonates decomposition and the SO₃ release gas.

Mineralogical analysis

Spectra of Figure 1 show that the kaolin is characterize

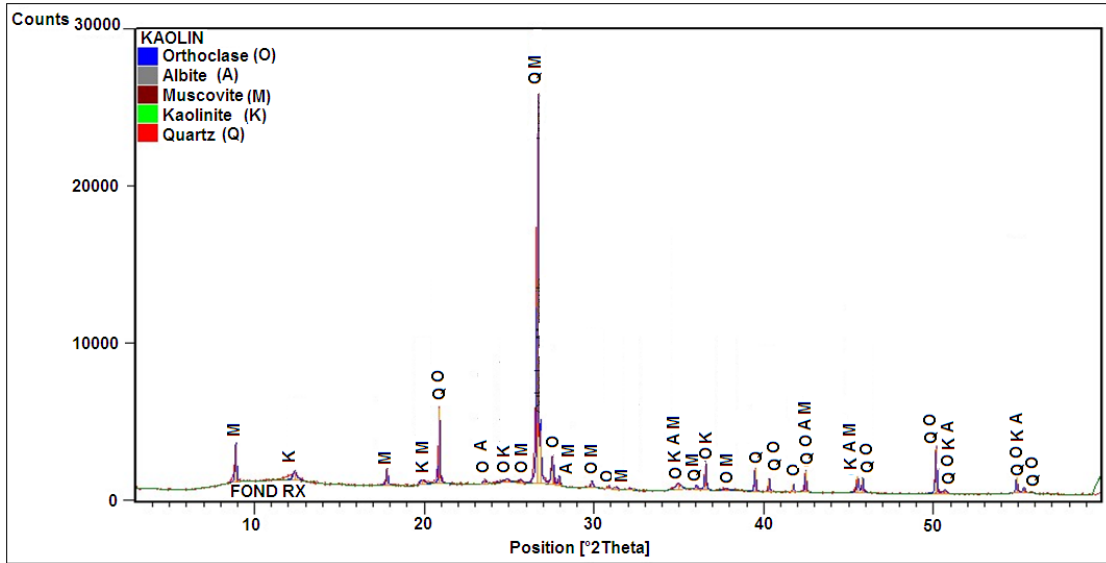


Figure 1. Mineralogical analysis of KAOLIN.

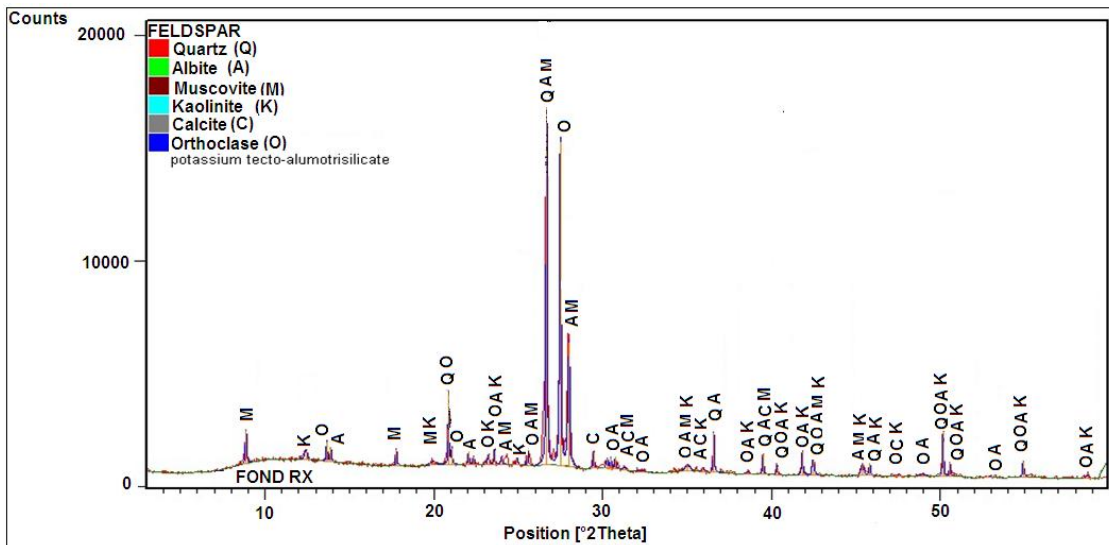


Figure 2. Mineralogical analysis of FELDSPAR.

by a predominance of quartz and muscovite elements. Figure 2 Feldspar shows a predominance of peaks belonging to quartz, feldspar and calcite. Elements were added during cooking for the formation of liquid phase which decreased the porosity of product. The mineral muscovite is also present; belonging to the family of mica which has the ability to resist chemical attack, thermal and participates dielectric properties of materials (Encyclopedie-gratuite/muscovite, 2013). The spectra of Figure 3 corresponding to the clay minerals show a predominance of calcite and illite. The high levels of iron in the clay comes from the illite which is a type of

glaucanite: illite, rich in iron (Ctmnc, 2009). The spectra of sand analyze shows a predominance of quartz with spectra belonging to the feldspar accompanied by calcite trace. The grinding efficiency and the reduction of apparent size of the crystallites were also followed by X-ray diffraction (Naimi, 2006).

Granulometric analysis

Particle size analysis by the pipette "Robinson" has provided the following fractions rates: clayey particles 64,

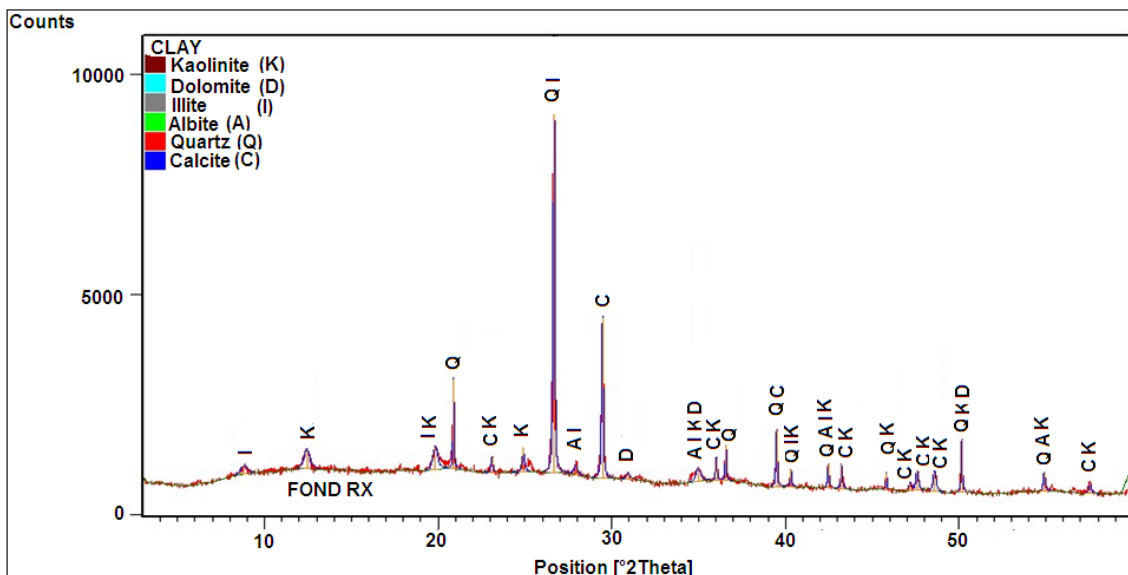


Figure 3. Mineralogical analysis of CLAY.

Table 2. Masses compositions.

Mixtures contents (%)	M ₁	M ₂	M ₃	M ₄	M ₅
Clay	55	55	55	55	55
Kaolin	30	28	26	24	22
Feldspar	10	12	14	16	18
Sand	05	05	05	05	05

dust particles 30.73 and sand particles 5.27%. We notice that the clay particles are predominant, which enables the deduced of clay plastic enough to cause a delicate drying. However, adding a degreaser is necessary to avoid any sensitivity to drying.

Technological parameters

The mixtures of contents are presented in Table 2. The research protocol is based on 05 mixtures types (M1, M2, M3, M4 and M5). Kaolin substitution was made by feldspar. The contents of this latter are: 10, 12, 14, 16 and 18% respectively). The viscosity is determined using a Ford Cup of 4 mm diameter, by measuring the flow time with 100 ml of suspension. The suspension was dried in a drying oven for 24 h at 110°C and then ground into powder with three different grain sizes (0.25 to 1 and 1.25 mm).

Rheological parameters

By considering values of refusal of each mixture, we

found out that the last mixture decreases remarkably with increasing milling time. Only mixtures M3 and M4, respond to the requirements of manufacturing a ceramic tile for a milling time of 1 h 30 min. The values are 7.10 and 5.43% respectively. Refusal values are quite low due to amorphization of the material, followed by formation of particles of smaller sizes, structural changes and dislocations, case observed for M5 for a milling time was 2 h 30 min. Refusal values, density, viscosity and thixotropy for 05 mixtures are presented in Figures 4 to 7 respectively. Refusal values are quite low due to amorphization of the material, followed by formation of particles of smaller sizes, dislocations and structural modifications case observed for C5. Refusal values, density, viscosity and thixotropy for 05 mixtures are presented in Figures 4, 5, 6 and 7.

Figure 5 shows a decrease in density for a milling time of 2 h, then. A further grinding, provides finer grains which stick together giving hardly castable fluids. The decrease in density values is not significant and is within the range of standards for manufacturing ceramic tiles.

For more energy saving, the grinding time of 1 h 30 min is recommended. The viscosity values vary in a similar way to that of the density values. The minimum values

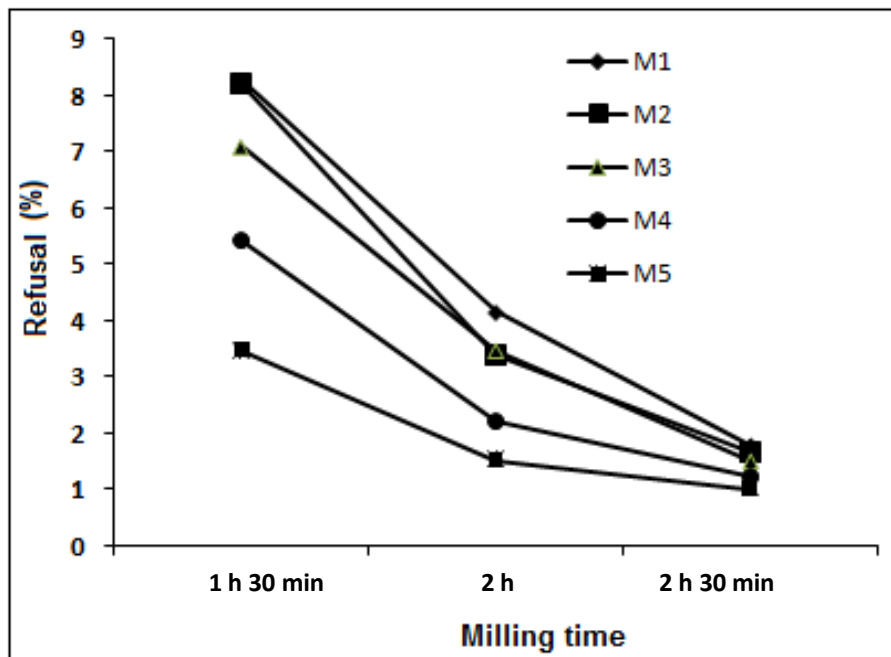


Figure 4. Variation of the refusal with milling time.

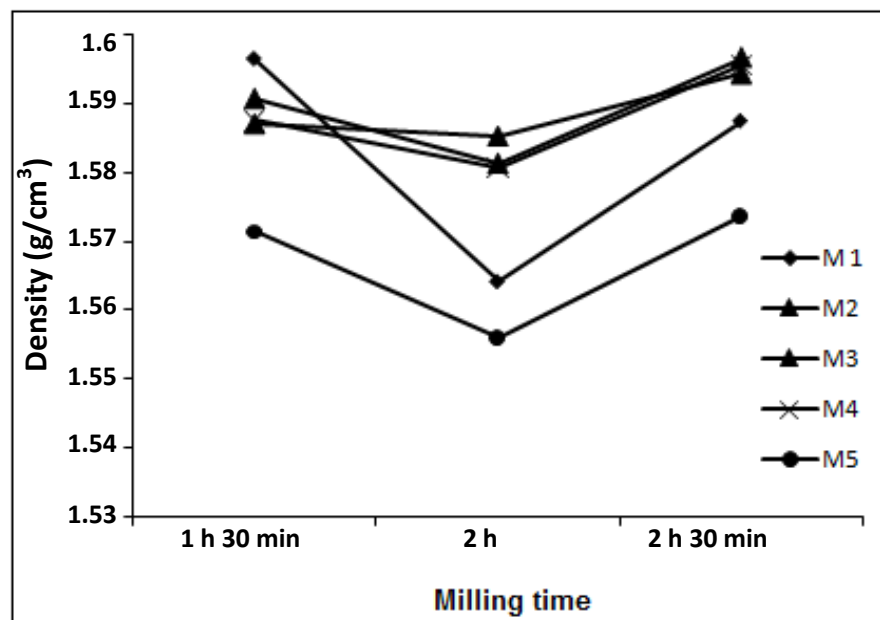


Figure 5. Variation of the density with milling time.

are 14 s and maximum values are about 16 s. The suspensions obtained present good flows. Almost all argillaceous barbotines of casting used in the ceramic industry are more or less thixotropic. They present a flow facilitated by stirring (Hausonne et al., 2005).

Suspension is complete when no particle remains in

the bottom of the tank or on the surface of the liquid. For a good stability and good suspension flow, the heavy coarse particles must be detached from the bottom, form deposit and total number of particles remains steady by time (Zwietering, 1958; Kendall and Stainton, 2001). In wet milling, the yield is much higher. An energy saving

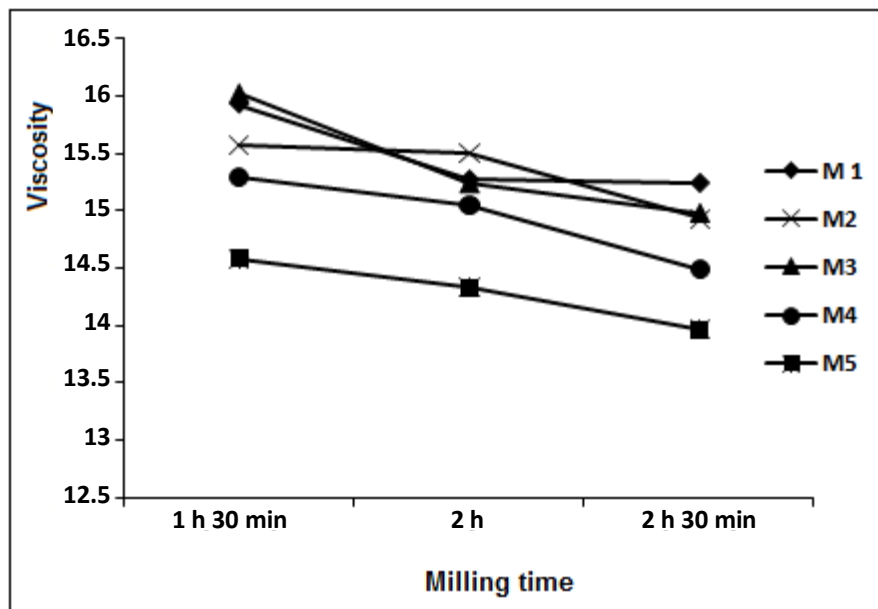


Figure 6. Variation of the viscosity with milling time.

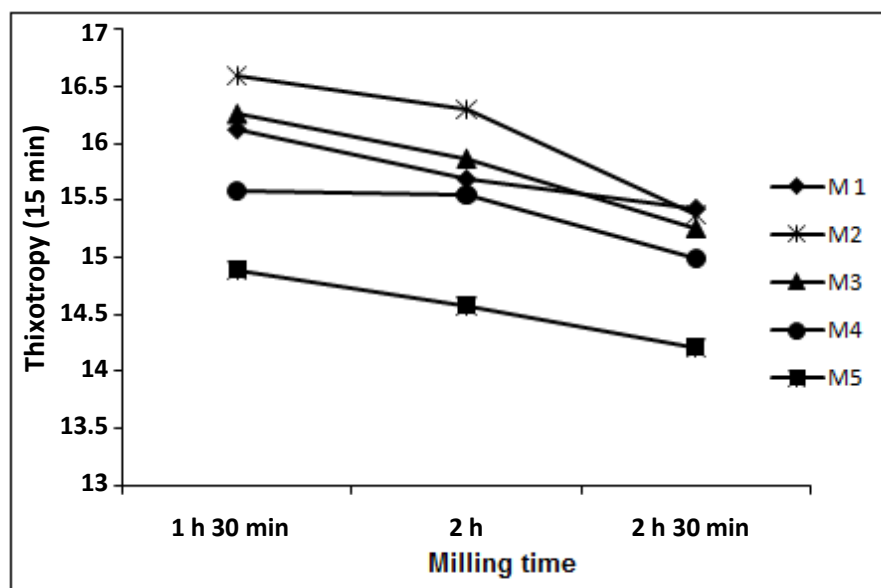


Figure 7. Variation of the thixotropy with milling time.

gain of at least 30% should be considered. If the material must be dried after grinding, it is clear that the labor cost by wet grinding will be much higher (Euroforum, 2009).

Physical and mechanical characteristics of dry and fired products

Considering the main physico- mechanical characteristics

of M3, M4 and M5, we notice that the values of the open porosity for the mixture M3 vary proportionally in relation to the grain size. This case is observed for 03 grain sizes, because the amount of liquid phase produced is in the optimum proportions which allow good wetting of the grains. For mixtures M4 and M5 porosity, there was an increase for a grain size of 1 mm and then decrease for a grain size of 1.25 mm. In this case, the liquid phase obtained as a function of addition is larger but does not

Table 3. Chemical composition of tesson obtained from three mixtures

Mixtures	Éléments										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	Loss ignition
M ₃	66.32	16.00	449	6.17	1.49	0.02	3.04	1.03	0.42	0.59	0.43
M ₄	66.14	16.19	452	6.10	1.48	0.03	3.11	1.07	0.43	0.58	0.36
M ₅	66.25	16.02	446	6.04	1.47	0.01	3.15	1.27	0.43	0.57	0.33

permit a good wetting of the grain size of 1 mm. For a little more advanced grinding (size 1.25 mm), the surface tension of grains increases, while the approximation mechanism up and connection is easily conducted. Also observed, is the decrease in porosity accompanied by decrease in absorption values. We must underline that the materials morphology obtained after sintering is largely conditioned by the powders size and their treatment. The porosity can take extremely variable forms. High porosity has a negative influence on the material strength (Kurz et al., 1995).

Chemical composition tesson of mixtures M3, M4 and M5

By considering the chemical compositions values of tesson fired mixtures M3, M4 and M5 in Table 3, we notice that mixture M3 contains more SiO₂. The presence of SiO₂ therefore, causes the breakdown of current capillaries causing a decrease in absorption values (Lemougna, 2004). This case is well justified by physicochemical mechanisms values obtained in this study. By a comparative study between the three mixtures, we notice that the best properties are provided by the mixture M3 for a grain size of 1.25 mm. Furthermore, we find that for the three types of grain, there is a decrease of absorption values which is due to the increase of gresification rates. The shrinkage values on products (dried, cooked), the values of porosity, absorption and flexural strength of the products (raw products, dry and cooked) are respectively as follows: [(2.65 to 4.29%) - (14.24 to 7.09%) - (10.69 Kgf / cm², 46.08 kgf / cm² - 234,47Kgf / cm²)]. By virtue of their durability, their enamel, particularly scratch resistant, low porosity, and feldspathic ceramics are well adapted to applications in the domain of ceramic tiles. The feldspar rate in the mixture is 3 to 14%. The mineralogical source of feldspar is a factor determining the technological and mechanical properties of sintered products. The composition M3 answers this (Boch, 2001).

Conclusions

The main results provided by this study are:

(a) Feasibility. It is possible by this technique in a few hours of grinding, to obtain a powder with grains of

several tens of millimeters from a mixture intended to elaborate ceramic tiles having grain initially enough coarse.

(b) Identification of parameters governing this process are three forms: the duration of milling, grain size and the solid charge of barbotines. Thus, it is possible to prepare the necessary barbotines to shape, right in the middle of implementation, that is, the size reduction is performed directly in the medium (liquid and adjuvant) used for the shaping. The rheological parameters study shows that the best values are obtained with mixtures M3, M4 for a grinding time of 1 h 30 min. Moreover, one notices a considerable decrease in the value of refusal, for mixing M4 relative to the mixture M3. This is due to amorphization of the milled powder. To this effect, we carry our gaze on the results of the mixture M3 compared to the results of the rheological properties. The study of physico-mechanical properties of uncooked, dried and cooked for its products shows that the best values are those obtained with the mixture M3 having a grain size of 1.25 mm. Granulometry of studied samples is excellent for use in the ceramic tiles manufacture.

Conflict of interest

The author has not declared any conflict of interest.

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