THE ELECTRONIC STRUCTURE PROPERTIES OF MONOLAYER TRANSITION

METAL CYANIDES

THESIS

Presented to the Graduate Council of Texas State University-San Marcos in Partial Fulfillment of the Requirements

for the Degree

Master of SCIENCE

by

Craig Higgins, MS

San Marcos, Texas August 2010

COPYRIGHT

By

Craig Higgins

2010

To My Hometown of New Orleans

ACKNOWLEDGEMENTS

I want to thank Dr. Byounghak Lee for his guidance in putting this thesis together, Dr. Carl Ventrice for getting my foot back in the door, and the other faculty, staff, and students of Texas State for all their knowledge, encouragement and support.

This thesis was submitted on May 19th, 2010.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	 	v

LIST OF FIGURES	vii
-----------------	-----

CHAPTER

I.	INTRODUCTION	1
II.	THEORETICAL METHODS	9
III.	NICKEL CYANIDE	20
IV.	IRON-DOPED NICKEL CYANIDE	29
V.	OTHER TRANSITION METALS	43
VI.	SUMMARY	60

LIST OF FIGURES

Figure	Page
1. L	ocalized d-orbitals ¹ situated in their respective axes2
2. E	nergy splitting for an octahedral coordinate complex2
3. SI	ketch of octahedral and square planar coordinate complexes
4. D de	biagram of U-tube set-up used in experiment. Each test tube has one reagent in e-ionized water4
5. T	he dehydrated XRD results ^{1v} for Ni ₂ (CN) ₄ 6
6. T	he dehydrated XRD results ^{1V} for FeNi(CN) ₄ 7
7. T	he DOS for a material with defined valence and conduction regions14
8. B	and structures for semiconductor/insulator and metal15
9. (A di er	A) The energy dispersion of a free particle. (B) The energy dispersion of a one- imensional lattice with lattice constant \mathbf{a} , including the forbidden region of nergy defined by the band gap E_g
10. TI (d	he FCC Brillouin zone lattice featuring high symmetry k-points ⁷ , and a silicon liamond structure) band structure along the high symmetry k-points17
11. D	FT process flow of calculations for DOS, band structure, and partial charge18
12. (A ur st	A) A five-atom theoretical structure used by Mo, Kaxiras ¹⁰ . (B) The 20-atom nit cell used in the thesis and reported experimentally. (C) The electronic band ructure for atomic structure (A). Note the electronic band gap of \sim 2eV20
13. Tl po	he ground-state total energy per atom as a function of lattice constant, with olynomial equation for minimum lattice constant
14. Co di	omparison of scaling factors for experimental, theoretical, other inter-atomic istances

 Convergence test of total energy per atom with increasing number of k-point meshes. 8x8x2 chosen for both accuracy and calculation speed
16. Breakdown of DOS into total, s, p, and d orbitals. The DOS are all at the same scale
17. The 3d-subshell of nickel, showing its electrons oriented into orbitals24
18. The d-orbital splitting for Ni atoms
19. The square planar Brillouin Zone, where $\mathbf{a} = $ lattice constant
20. Band structure of Ni ₄ (CN) ₈
21. Band structure of $Ni_4(CN)_8$, the contribution of each Ni d-orbital highlighted28
22. Molecular structure of Ni ₂ Fe ₂ (CN) ₈ . Iron ions replace nickel at nitrogen-centered coordinate complexes
23. Breakdown of orbital behavior for iron 3d-subshell. The first 5 electrons fill one spin of each orbital, with the d_{xy} orbital completely filled
24. Hypothetical DOS before and after ionization with Fe (+4 q_e)
25. Holes are formed as electrons move from the valence to the conduction band. E_f should shift down, leaving the top of valence band partially occupied32
26. Comparison of original experimental inter-atomic distances with $Ni_2Fe_2(CN)_8$ 32
27. 20-atom unit cell for Ni ₂ Fe ₂ (CN) ₈ , for both anti-ferromagnetic and ferromagnetic cases
 28. (A) DOS split into majority- (up) and minority (down) spins for the ferromagnetic-ordered Fe ion configuration. (B) Expanded view of the spin-resolved density of state near the Fermi energy, E_f
29. The decomposition of the FM minority-spin d-orbitals and orbital splitting35

30.	Majority and minority spin-polarized band structures for FM, Ni ₂ Fe ₂ (CN) ₈ E _f is 0eV
31.	Band indicies crossing E_f in minority spin for FM Ni ₂ Fe ₂ (CN) ₈ are 51 and 52, and are partially occupied
32.	Contributions of the d-orbitals for Ni and Fe around E_f , FM case. The principal contributions are from d_{yz} and d_{xz}
33.	Total and expanded view of DOS for the anti-ferromagnetic case, $E_f = 0eV$ 38
34.	DOS is broken down into d-orbital contributions
35.	Band structure of the AFM case
36.	Band indices 54 and 55 cross E_f and are partially occupied, contributing metallicity
37.	The contribution of the Ni and Fe d-orbitals in the band structure for the AFM case
38.	The electronic configurations of transition metal elements along Period 4 of the periodic table, along with total # of electrons for each new 20-atom unit cell43
39.	Chart of relative stabilities of transition metals along Period 4. The last two columns list calculated magnetic moments for FM and AFM configurations44
40.	Plots of (A) the relative energy stabilities of transition metal cyanides, and (B) their corresponding temperature differences
41.	Comparison of FM and AFM magnetic moments with expected valences45
42.	3d-subshell orbitals for Manganese46
43.	Comparison of inter-atomic distances, original Ni ₄ (CN) ₈ vs. Ni ₂ Mn ₂ (CN) ₈ 47

44.	(A) DOS split into majority- (up) and minority (down) spins for the ferromagnetic-ordered Mn-doped structure, and (B) expanded view of the spin-resolved density of state near the Fermi energy, $E_{\rm f}$
45.	d-orbital splitting at the Fermi level for Ni ₂ Mn ₂ (CN) ₈ , FM case, minority spin48
46.	The spin-resolved FM band structures for the majority and minority spins of Mn- doped nickel cyanide
47.	A close-up of Mn-doped minority spin FM band structure near E _f , showing partially occupied band indices
48.	Illustration of minority spin d-orbital contributions near E_{f}
49.	The Mn-doped AFM DOS both (A) for $\pm 4eV$, and (B) a more localized expanded view near E_{f}
50.	The AFM d-orbital splitting behavior for $Ni_2Mn_2(CN)_8$
51.	(A) Mn-doped AFM band structure, and (B) expanded band indices near zero energy
52.	Illustration of AFM band structure d-orbital contributions near zero energy53
53.	The electron configuration and d-orbitals filled for Ti
54.	The comparison of inter-atomic distances for the experimental and Ti-doped lattice constants
55.	In (A) the total DOS and (B) expanded view of DOS for $Ni_2Ti_2(CN)_8$, spin-resolved FM case
56.	The d-orbital splitting for the majority spin FM DOS56
57.	The spin-resolved FM Ti-doped band structures for the majority and minority spins

58.	A close-up of the Ti-doped minority spin FM bands near zero energy, which shows no partially occupied bands
59.	The (A) total DOS and (B) expanded view of DOS for Ni ₂ Ti ₂ (CN) ₈ , spin-resolved AFM case
60.	The d-orbital splitting for the majority spin AFM DOS58
61.	The AFM Ti-doped band structure, and (B) bands close to zero energy

-

CHAPTER I

INTRODUCTION

Transition metal cyanides are molecules consisting of coordinate complexes featuring a transition metal ion in the center of four or six cyanide (CN-) molecules. In the periodic table, the transition metals are part of Group B elements, taking up the middle of the table and including periods 4-7¹. Most transition metals are found naturally in compound form, and due to their bright colors are often used as pigments. CN- is a rod-like molecule with a hybridized s-p bond between the component atoms, allowing it to assume this shape and leaving only a single charge available for bonding. In transition metal cyanides CN- takes the form of a ligand, or a bound donor molecule which serves as an anion, forming hybridized bonds with the transition metal cation².

For transition metals the d-orbitals, or pairs of electrons in the d-subshell, and as such behave according to ligand field theory, which deals with the distribution of dorbitals both in how they achieve minimum repulsion with each other in addition to interacting with other bonding orbitals. Fig. 1 shows the constant amplitude surface of these orbitals. The behavior of the d-orbitals in the transition metal ions is dependent on the symmetry and type of ligands present. In octahedral and tetragonal structures there is an energy difference Δ_o between the lower energy orbitals, commonly referred to as t_{2g} , and the higher energy e_g orbitals³.



Fig. 1 Localized d-orbitals¹ situated in their respective axes.

Fig. 2 shows the energy splitting for an octahedral coordinate complex. As CN- is one of the earliest members of the spectrochemical series, this difference Δ_o can be great.



Fig. 2 Energy splitting for an octahedral coordinate complex.

The square planar coordinate complex is similar in structure to that of the octahedral complex, in that both have four ligands residing on the axes of the system in the same xy-plane and along the xy-axes. The main difference between the two is the square lattice does not have two ligands attached along the z-axis. The result is that of the five d-orbitals $d_{x^2-y^2}$ shows the strongest repulsion from the bonding ligands it shares its axes with while the d_{z^2} orbital has no repulsion since there is no opposing ligand. Any transition metal cation with a d⁸ configuration³, such as nickel, will prefer to take this geometry. It should also be pointed out that for the square planar lattice very weak van der Waals bonding is evident in the z-axis direction, where there are no bonding ligands to cause repulsion. Fig. 3 shows a comparison between the octahedral and square planar complexes.

Nickel cyanide has seen significant attention of late due to the nature of this planar bonding, some seeing it as an analogue for graphene. The high carrier mobility and molecular thickness of graphene makes it an ideal candidate for nano-scale devices.



Fig. 3 Sketch of octahedral and square planar coordinate complexes.

As it is difficult to make in large molecules, an alternative material with the same properties could be very useful.

Some recent work⁴ on both hydrated and dehydrated transition metal cyanides explored the electronic and chemical properties of these structures. Reagents used in the experiment included tetracyanonickelates, hexacyanochromates, and transition metal sulfates. These were placed in a U-tube set-up, as shown in Fig. 4. Two rubber-sealed test tubes are attached by another tube placed through the seals.



Fig. 4 Diagram of U-tube set-up used in experiment. Each test tube has one reagent in de-ionized water.

Within the test tubes are the separate reagents suspended in de-ionized water or some other liquid. The tubes were placed in a vacuum oven and heated at 42°C (315K) at atmospheric pressure for a three-week period. The nickel cyanide crystals then form at the top of the connecting tube. The stoichiometry for the creation of the nickel cyanide is

$$NiSO_4 \bullet 6H_2O + K_2Ni(CN)_4 \bullet 2H_2O \rightarrow Ni_2(CN)_4 + K_2SO_4 \bullet 8H_2O.$$

Likewise, the iron-doped variant FeNi(CN)₄, one with the nickel ions in the nitrogen-centered coordinate complexes, were created in the same manner using this relationship

$$K_2Ni(CN)_4 + Fe(NH_4)_2(SO_4)_2 \rightarrow FeNi(CN)_4 + K_2(NH_4)_2(SO_4)_2$$

Once these crystals were synthesized, they were then examined via powder x-ray diffraction (XRD) in both hydrated and dehydrated powder forms. In the hydrated cases the reagents were dissolved together in water, ethanol, and octyl pyrrolidone. The reagents formed precipitates, and these were then centrifuged to remove excess liquid. The dehydrated samples were created by heating precipitates on a hot plate at a constant temperature 200°C (473K), then analyzed. From powder XRD the inter-atomic distances can be determined via the intensity of the peaks at 20 or the diffraction angle at a particular crystal plane.

Results from d-spacing, or the distance between crystal planes, for all samples were nearly the same regardless of hydration. Figs. 5 and 6 show the dehydrated XRD results for the nickel- and nickel-iron cyanides show the d-spacing at the largest peak intensity, which for $Ni_2(CN)_4$ was 4.374Å at 20.29° while for FeNi(CN)₄ was 4.760Å at 18.63°.

While the experiment revealed some interesting physical properties of the partially dehydrated nickel cyanide and its Fe-doped counterpart, they don't tell us anything about the electronic structural properties. This thesis is an attempt to examine via an *ab initio* or quantum first principles study the general characteristics of monolayer transition metal cyanides.



Fig. 5 The dehydrated XRD results^{iv} for $Ni_2(CN)_4$.



Fig. 6 The dehydrated XRD results^{iv} for FeNi(CN)₄.

This structure is examined using analysis tools common to this kind of study resulting from calculations performed using density functional theory (DFT), including density of states (DOS) and electronic band structure analysis. After examining nickel cyanide, other transition metal ions are used to replace nickel at nitrogen-centered sites in the crystal. These new structures are examined using the same techniques. The nature of bonding between the d-orbitals of the transition metal ions and their CN- ligands is considered, and magnetic moments are introduced into the study to determine the relative stability of ferromagnetic vs. anti-ferromagnetic cases as a function of the energy/temperature.

 \sim

CHAPTER II

THEORETICAL METHODS

DFT is an *ab initio* computational approach to find the ground state energy of electronic configurations. The quantum mechanical approach considers the wave function Ψ of a system⁵. For a single body problem that deals with an electron moving in a potential v(r), the wavefunction equation takes the form of,

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v(\mathbf{r})\right] \Psi(\mathbf{r}) = \epsilon \Psi(\mathbf{r}).$$

For a many body problem that involves several electrons, the construction of the wave function becomes considerably more complicated. The wavefunction includes the electron-electron interaction,

$$\left[\sum_{i}^{N} \left(-\frac{\hbar^2 \nabla_i^2}{2m} + v(\mathbf{r}_i)\right) + \sum_{i < j} U(\mathbf{r}_i, \mathbf{r}_j)\right] \Psi(\mathbf{r}_1, \mathbf{r}_2 \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2 \dots, \mathbf{r}_N),$$

where,

$$\hat{U} = \sum_{i < j} U(r_i, r_j) = \sum_{i < j} \frac{q^2}{|r_i - r_j|},$$

is the Coulomb interaction. In general, the quantum approach requires the specification of v(r). The solution of the Schrödinger equation yields the observables as the expectation values of the corresponding operators,

$$v(r) \Rightarrow \Psi(r_1, r_2, \dots, r_n) \Rightarrow n(r)$$

One of the observables that can be calculated is the particle density,

$$n(\mathbf{r}) = N \int d^3 r_2 \int d^3 r_3 \dots \int d^3 r_N \Psi^*(\mathbf{r}, \mathbf{r}_2 \dots, \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2 \dots, \mathbf{r}_N).$$

In density functional theory, the external potential v(r) is uniquely specified by the ground-state charge density. To summarize,

$$n(r) \Rightarrow \Psi(r_1, r_2, \dots, r_n) \Rightarrow v(r)$$

Therefore DFT enables us to derive all the relevant physical quantities from the ground-state density. The effect is to take a problem with many variables, such as the many-body wavefunction $\Psi(r_1, r_2, ..., r_n)$, and covert it into one dependent on a single variable, the particle density n(r). This makes a previously complicated and computationally expensive problem feasible.

DFT is based on two essential bodies of computational thought: the Hohenberg-Kohn theorem and Kohn-Sham equations. Hohenberg-Kohn states that the total energy of a system of interacting particles can be related to its charge density. Given a groundstate density, there is a corresponding ground-state wave function that minimizes the energy expectation value.

$$E_{v,0} = \min_{\Psi \to n_0} \langle \Psi | \hat{T} + \hat{U} + \hat{V} | \Psi \rangle_{.}$$

Here, $E_{\nu,0}$ is the ground state energy for the potential v(r), and for a given ground state charge density $n_0(r)$ there is a ground state wave function Ψ_0 that minimizes this energy. From the variational principle, the total-energy functional $E_{\nu}[n]$ can be minimized with respect to n.

 $E_{v}[n]$ can thus be written as

$$E_{v_0}[n_0] = \min_{n \to n_0} \left[\min_{\Psi \to n} \langle |\hat{T} + \hat{U} + \hat{V}| \rangle \right],$$

or

$$E_{v_0}[n_0] = \min_{n \to n_0} \left[E_v[n] \right] = \min_{n \to n_0} \left[T[n] + U[n] + \int d^3 r \ n(r) \ v(r) \right]$$
$$= \min_{n \to n_0} \left[T[n] + U[n] + V[n] \right].$$

Here the potential v(r) is independent of the operators for kinetic- and electron-electron interactions. However, the exact energy functional is not known except in the trivial homogeneous gas case.

In Kohn-Sham, single-particle wave functions are employed for both the particle density and many-body effects are included in the exchange-correlation functional. One useful modification is to the kinetic energy functional T[n]. It can be decomposed into one part that represents non-interacting particles $(T_s[n])$, and the remainder $(T_c[n])$. The

electron-electron functional U can likewise be broken down in a similar manner, and the result is another way of writing the exact-energy functional as

$$E[n] = T[n] + U[n] + V[n] = T_s[\{\phi_i[n]\}] + U_H[n] + E_{xc}[n] + V[n]$$

Here, $T_s[\{\varphi_i[n]\}]$ expression denotes the single particle orbitals' contribution to the kinetic energy and E_{xc} represents the exchange-correlation energy, which contains all the many-body aspects of the calculation, both the kinetic energy and Coulomb reaction. In practice, E_{xc} is represented using a local density- or gradient-based approximation.

The local density approximation (LDA) can be used to obtain the approximate exchange-correlation energy. For the exchange energy $E_x[n]$, the exact value can be calculated for homogeneous electron gases with electron density *n* as,

$$E_x^{LDA}[n] = -\frac{3q^2}{4} \left(\frac{3}{\pi}\right)^{1/3} \int d^3r \, n(\mathbf{r})^{4/3}.$$

The exact correlation energy $E_c[n]$, is unknown and is approximated using the result of more complicated, with Quantum Monte Carlo (QMC) calculations. The LDA for $E_{xc}[n]$ is

$$E_{xc}^{LDA} = \int d^{3}r \; e_{xc}^{hom}(n)|_{n \to n(r)} = \int d^{3}r \; e_{xc}^{hom}(n(r)).$$

where e_{xc}^{hom} is the total per-volume exchange-correlation energy of a homogenous electron liquid. The effect is to make e_{xc}^{hom} a function of the charge density, exploiting the density at **r**. LDA can also be written as a spin-polarized calculation, taking into

account the spin degrees of freedom, which is known as local spin density approximation (LSDA).

$$E_{xc}^{LSDA}[n_{\uparrow},n_{\downarrow}] = \int d^{3} r n e_{xc}^{unif}(n_{\uparrow},n_{\downarrow}).$$

As any system has spatially-varying particle density, LDA is not always the best choice to mimic this behavior, and there is another approach which is very useful. The generalized gradient approximation (GGA) is a semilocal functional which mimics E_{xc} as

$$E_{xc}^{GGA}[n] = \int d^3r \ f(n(\boldsymbol{r}), \Delta n(\boldsymbol{r})).$$

The choices of function $f(n, \nabla n)$ can create different GGAs. Because of the inclusion of the gradient dependence, GGA works better than LDA in inhomogeneous systems. GGA tends to give good results for most molecular bonds such as σ or π bonds but doesn't do as well for weaker inter-atomic forces such as van der Waals bonding. In the case of spin-polarized calculations, GGA can give better approximations for the exchangecorrelation energy than LSDA, improving on total energies, energy barriers, and structural energy differences⁶. The Perdew-Burke-Ernzerhof (PBE), improves over earlier approximations by simplifying the functional.

Analysis: Density of States and Electronic Band Structure

Density of States: DFT is used to calculate the electronic properties of a system, such as the density of states (DOS) and the electronic band structure. Formally, DOS is defined as

$$D(\omega) = \sum_{i} \delta(\omega - \varepsilon_{i}) = \sum_{n} \int \frac{d^{3}k}{4\pi^{3}} \,\delta(\varepsilon - \varepsilon_{n\vec{k}})$$

Here, ε_i are the eigenvalues of the system. DOS is the number of electron states available to be occupied, as a function of energy. The highest energy level where states have a 50% chance to be occupied is called the Fermi level, or E_f .

At zero temperature (T = 0K) E_f is the same as the chemical potential μ , which is defined,

$$\mathbf{n} = \int \frac{d^3k}{4\pi^3} f(\varepsilon_{\vec{k}}),$$

where **n** is the number of electrons and $f(\varepsilon_k)$ is the Fermi-Dirac distribution,

$$f(\varepsilon_{\overrightarrow{k}}) = \frac{1}{e^{(\varepsilon_k - \mu)/k_B T} + 1} .$$

The valence band is the band whose energy lies below the Fermi energy while the band above the Fermi level is called the conduction band.



Fig. 7 The DOS for a material with defined valence and conduction regions.

For insulators and semiconductors, the valence bands are completely occupied and the empty conduction bands are separated by the band gap, as seen in Fig. 7. As a convention, all plotted states' energy is shifted by E_f so the top of the valence band is at zero.

Band Structure: In crystals, the combined molecular orbitals split and form groups of electron states so numerous and so close together as to be thought of as energy bands. Material can be classified based on band structures: insulators/semiconductors and metals. In both insulators and semiconductors the valence bands are completely filled up to the Fermi level and unfilled above it. This relationship is shown in Fig. 8. The difference between the two is that insulators generally have a wider gap while semiconductors have a much smaller gap, even containing a partially filled band or two in the transitional region. In a metal, some energy bands are partially filled, crossed by the Fermi level and with no definable band gap.



Fig. 8 Band structures for semiconductor/insulator and metal.

It is this difference in electronic structure that determines the transport properties of the respective materials, with metals and insulators/semiconductors having increasing and decreasing resistivity with increasing temperature, respectively.

The periodicity of crystals gives rise to periodicity of the potential in the Schrödinger equation⁷. Were an electron to travel freely, its energy could be plotted as a function of the wave-vector k, which is related to a particle's momentum p as: $k = \hbar p$. Here, \hbar is $(h/2\pi)$, or the Planck constant divided by 2π . Energy is a continuous function of k with the dispersion of $(\hbar k)^2/2m$. In the presence of periodic potential, however, the good quantum number is not the particle momentum but the crystal momentum.



Fig. 9 (A) The energy dispersion of a free particle. (B) The energy dispersion of a one-dimensional lattice with lattice constant \mathbf{a} , including the forbidden region of energy defined by the band gap E_g .

Because of the periodicity of the crystal, k is limited within $a/2\pi$, where a is the lattice vector of the crystal. This variable defines an alternate framework of calculations commonly known as "k-space" or wave-vector space. Band gaps appear at the zone

boundary, $\pm \frac{\pi}{a}$, with discontinuity in the density of states (a.k.a. van Hove singularity), as seen in Fig. 9. This region in k-space is known as the Brillouin zone (BZ).

In Fig. 10, the DFT band structure of silicon (Si) is plotted along a set of high symmetry k-points, revealing an ~1.0eV band gap. The actual band gap of Si is 1.12eV.



Fig. 10 The FCC Brillouin zone lattice featuring high symmetry k-points⁷, and a silicon (diamond structure) band structure along the high symmetry k-points.

Computational Software and Calculation Procedure:

The software package used in this thesis for all calculations was the Vienna Ab-Initio Simulation Package, or VASP⁸. VASP uses pseudopotentials and a plane wave basis set to perform *ab initio* electronic structure and molecular dynamics calculations. It solves the Kohn-Sham (KS) to calculate DFT ground-state energy using an iterative method, often referred to as a self-consistent (SC) approach⁹. This method has been proven effective in dealing with such diverse properties as the ground states of liquid and simple metals, metal-nonmetal transitions, and phonon dispersion relations in insulators and metals. To determine the properties of a given system, the process flow shown in Fig. 11 was used. Input files covering the size of the simulation cell, atomic coordinates within the cell, a *k*-space mesh, and the pseudopotentials corresponding to the atom types were created. The positions of atoms in the unit cell were relaxed using a conjugate gradient (CG) method. CG is an iterative process where the KS ground state energy is minimized along a given search direction, the direction of the calculated forces and the stress tensor. Then, after the energy and associated forces are re-calculated, the minimum of the total energy is found from an interpolation, with a correction step applied to improve the line minimization in a particular direction. The process continues, the new energy and forces building on the previous atomic positions, until a converged total energy value is reached, yielding a minimum lattice constant value.



Fig. 11 DFT process flow of calculations for DOS, band structure, and partial charge.

The new atomic configuration is now subjected to a self-consistent (SC) calculation from which the density of states can be evaluated. SC also yields updated charge density used as an input into band structure calculations, along with updated wavefunctions used to determine partial charges within a certain energy range. These tools complement each other, as DOS provides information about the concentration of available states and the band structure shows the dispersion of the energy, yielding properties such as effective mass, band splitting, etc.

CHAPTER III

NICKEL CYANIDE

Previous Work: For the same chemical compound of Ni:C:N=1:2:2, there are number of different possible atomic configurations. Previous research has investigated the behavior of this material to find the most stable atomic configuration for $Ni_4(CN)_8$. Mo and Kaxiras¹⁰ reported in a theoretical DFT study that $Ni_4(CN)_8$ in quasi-one-dimensional nanotubes is a semiconductor with a defined band gap of 2~3eV.



Fig. 12 (A) A five-atom theoretical structure used by Mo, Kaxiras¹⁰. (B) The 20-atom unit cell used in the thesis and reported experimentally. (C) The electronic band structure for atomic structure (A). Note the electronic band gap of ~2eV.

Fig. 12 (A) shows that the theoretical 5-atom unit cell, suggested as a result of a hypothetical gas-phase synthesis process, has its cyanide ligands oriented so that each central Ni atom is attached to two carbon and two nitrogen atoms apiece. This particular structure, however, has never been reported experimentally.

The atomic structure that we study in this thesis is shown in Fig. 12 (B). Although the ground state energy of this structure is higher than the structure shown in Fig. 12 (A) by 0.07eV/unit cell, the wet synthesis process favors the formation of a structure where one Ni atom is surrounded by 4 C atoms and the other Ni atom is surrounded by 4 N atoms in each unit cell. Yet another structure which includes the two Ni atoms are surrounded by either 3 C and 1 N or 1 C and 3 N has a higher grounded state energy by 0.1 eV/unit cell, and it is not observed in our experiments.

Computational Parameters: We used the Perdew-Burke-Ernzerhof (PBE)⁶ generalized gradient approximation (GGA) for the exchange-correlation functional and projected augmented plane-wave pseudopotentials.



Fig. 13 The ground-state total energy per atom as a function of lattice constant, with polynomial equation for minimum lattice constant.

During atomic relaxation the energy cut-off was set at 350eV and the Blöchl scheme⁸ was used for k-space integration. For the atomic configuration, the inter-atomic distances were relaxed via the conjugate gradient (CG) method. The lattice constant was determined by minimizing the total energy and it was found to be 9.6865Å, as seen in Fig. 13. Compared with the x-ray diffraction experimental data there is a significant difference in the inter-atomic distance and the size of unit cell. Whereas in the experiment N-Ni distance was more than 2Å, the minimum atomic configuration of our structure is nearly equal to that of the Ni-C bonding length.

Hibble, Chippindale, et al.¹¹, have in their study of multi-layer nickel cyanide suggested a model similar to the experimental data could exhibit such a marked shortening of its N-Ni distance by removal of H_2O molecules.

Ni ₄ (CN) ₈ Bonding Type	Exp. Inter-atomic Distances (Å)	Theo. Inter-atomic Distances (Å)	Inter-atomic Distance in Multi-layer Structure ^{iv} (Å)
Ni-C	1.870	1.836	1.886/1.860
C-N	1.150	1.172	1.150
N-Ni	2.010	1.835	2.052/1.860

Fig. 14 Comparison of scaling factors for experimental, theoretical, other inter-atomic distances.

As the partially dehydrated experimental data contains essentially the same interatomic distances as this multi-layer study, it stands to reason that dehydration to $Ni_4(CN)_8$ could cause the N-Ni ligand to contract to a length nearly equal to that of the Ni-C ligands. Fig. 14 compiles these results. Having found an ideal lattice constant with associated atomic coordinates, the new unit cell was then used as an input for selfconsistent calculations to determine the electronic and orbital behavior of the $Ni_4(CN)_8$ system. First, a few tests were conducted to create optimal computational parameters.

We tested k-point mesh to incorporate all wave functions within the BZ. After analyzing minimum energy states for successive meshes of increasing numerical density, an 8x8x2 mesh was selected, as seen in Fig.15.



Fig. 15 Convergence test of total energy per atom with increasing number of k-point meshes. 8x8x2 chosen for both accuracy and calculation speed.

The energy cut-off of the plane-wave in our self-consistent calculations was set to include 25% more wave-vectors than the highest wave-vector necessary for pseudopotentials. For magnetic systems we selected LSDA to include spin.

Analysis: Now the density of states was examined. First, the eigenvalues before and after the Fermi level were analyzed, and a band gap of 1.4eV was found. This result indicates that this material is a semiconductor. Fig. 16 shows the DOS broken into its total and local contributions for s, p, and d orbitals. From this plot, it can be determined that there are two large and very narrow peaks near the Fermi level for the d-orbital

decomposition. Its useful at this time to consider the fact that 3d-orbitals, being more localized than s and p, have more overlap and hence a narrower energy range. The peaks near E_f for the d orbital are narrow, a result which makes sense.



Fig. 16 Breakdown of DOS into total, s, p, and d orbitals. The DOS are all at the same scale.

And as only the nickel atoms in $Ni_4(CN)_8$ contain d, they are the contributors at zero energy. As seen in Fig. 17, the 3d-subshell of Ni has eight electrons, with five filling one spin and three in the other direction.

	Ni	ckel: [Ar] 3d	⁸ 4s ²	
d _{xy}	d _{yz}	d _{xz}	d _{z²}	d _{x²-y²}
41	41	41	4	4

Fig. 17 The 3d-subshell of nickel, showing its electrons oriented into orbitals.

According to ligand field theory³ the square planar lattice has four cyanide ligands in direct conflict with a transition metal ion center along its xy-planar axes. This geometry splits the degeneracy of the transition metal d-states. It is easy to see that the overlap between the each d-orbital and the (CN)⁻ ligand is in order of $d_{xy} < d_z^2 < d_{xz}=d_{yz}$ $< d_{x^2-y^2}^2$. Because the Coulomb repulsion is roughly proportionally to the square of the overlap between the wavefunctions, the energy level splitting follows the overlap between the d-orbitals and the ligands.

The DOS for the Ni d-orbitals are split and plotted in Fig. 18. As expected, the d_{xy} orbital has the lowest energy. The highest is $d_{x^2-y^2}$, which is up in the conduction region. Sitting at the Fermi level are the degenerate d_{yz} and d_{xz} , with d_{z^2} slightly beneath zero energy. The insulator behavior stems from the splitting of the d-bands. For nickel atom to fill 8 d-orbitals, d_{xy} , d_z^2 , d_{xz} , and d_{yz} are occupied, leaving the d_x^2 band unoccupied. Now the band structure is addressed, using the charge densities from the self-consistent run.



Fig. 18 The d-orbital splitting for Ni atoms.

Although LSDA was used for all calculations $Ni_4(CN)_8$ is a non-magnetic semiconductor and in calculations there was no differentiation between spins. The path chosen had the high symmetry points M, Γ , X, W, and Γ as seen in Fig. 19.



Fig. 19 The square planar Brillouin Zone, where **a** = lattice constant.



Fig. 20 Band structure of Ni₄(CN)₈.
In Fig. 20, the band structure is shown for the region around E_f , adjusted so the top of valence band (TVB) is set to zero. From this plot $Ni_4(CN)_8$ is a semiconductor a band gap of 1.7eV, and a number of thin, occupied bands 0.1eV beneath TVB. As in the DOS this energy range was previously associated with localized orbital behavior, its likely that these bands are composed of 3d-subshell orbitals from the Ni atoms.

The contributions of the five transition metal d-orbitals are found in Fig. 21. As in the DOS, the Ni d_{xy} has the lowest energy, occupying bands centered on -0.8eV. The d_{yz} and d_{xz} orbitals occupy the bands at zero energy, and in particular are degenerate at point Γ in the BZ. Slightly beneath the Fermi level is the d_{z^2} orbital, which is localized at -0.1eV, and the $d_{x^2-y^2}$ forms the bottom of the conduction band (BCB). From this orbital split we see that the Ni atoms, residing at the center of the square planar coordinate complexes which make up the lattice, make up the bands which are closest to zero energy, with only the $d_{x^2-y^2}$ orbital free to conduct charge, likely due to the strong repulsion along the xy-axes from the CN- ligands residing there.

In two dimensions the nickel cyanide proved to be a narrow-gap semiconductor whose nickel d-orbitals serve as potential contributors near zero energy. The DOS and band structure both showed that the d-orbitals associated with the z-axis were occupying the top of the valence band, and only the $d_{x^2-y^2}$ escaped into the conduction region, which is consistent with ligand field theory.



Fig. 21 Band structure of Ni₄(CN)₈, with the contribution of each Ni d-orbital highlighted.

CHAPTER IV

IRON-DOPED NICKEL CYANIDE

Iron-Doped Nickel Cyanide (Calculations and Plots):

Ni₄(CN)₈ proved itself to be a narrow-gap semiconductor with extremely strong bonding of atoms in its xy-plane. The CN- ligands are σ bonds, hybridized s-p orbitals where the bonding is a head-to-head overlap so that the electron density is along the bonding axis¹. Mo and Kaxiras¹⁰, in their paper on transition metal cyanide nanotubes, list the C-Ni-C bond in their structure as being σ bonding. As σ is the strongest of the covalent bonds, the Ni-C bonds are difficult to break. To alter the character of the material, only the nitrogen-centered coordinate complexes are candidates for ion replacement.



Fig. 22 Molecular structure of Ni₂Fe₂(CN)₈. Iron ions replace nickel at nitrogen-centered coordinate complexes.

Fig. 22 shows the 20-atom unit cell with this ion replacement. In the experiment⁴, a different composition of reagents yielded a new material with the iron ions replacing the nickels at the N-centered complex sites. Like nickel, iron is a transition metal element, lying in the periodic table along the same Period 4, in Group 8. However its 3d-subshell has only 6 electrons, with a typical arrangement as seen in Fig. 23. This changes the total number of electrons in the unit cell, from 112 to 108.

			2 . 4
ron	[Ar]	30	49
ILOH.	[m]	20	40

d _{xy}	d _{yz}	d _{xz}	d _{z²}	$d_{x^2 - y^2}$
41	4	4	4	4

Fig. 23 Breakdown of orbital behavior for iron 3d-subshell. The first 5 electrons fill one spin of each orbital, with the d_{xy} orbital completely filled.

As there are two fewer electrons occupying the 3d-subshell, it is likely that the nickel/iron cyanide will have different electronic properties from the chemically neutral nickel cyanide.

In replacing the transition metal ions at the nitrogen-centered coordinate complex sites, it is useful to look at the difference in electronic configurations of Ni and Fe atoms. In our 20-atom Ni₄(CN)₈ unit cell, there are 8 CN- molecules each with a -1 q_e effective charge, giving a total charge of -8 q_e , where q_e is the charge of one electron. The nickel ions each contain a +2 q_e .

4 [Ni(+2)] + 8[CN(-)] = neutral

An iron atom has two fewer 3d⁶ electrons than a nickel atom and, when doped at nitrogen neighbor sites, each iron atom provides 2 holes to the system.

$$2 [Ni(+2)] + 2 [Fe(+4)] + 8 [CN(-)] = +4 (excess holes)$$

Because of this change in the electronic configuration, we are left with a +4 charge for the 20-atom unit cell. A hole is just a vacant orbital in an energy band, acting as a positive charge⁷ q_e . The DOS and band structure should reflect this development. Provided the band structure remains unchanged by the doping of irons, E_f should shift to a lower energy. Fig. 24 shows the Fermi level shift illustrating this concept for DOS.



Fig. 24 Hypothetical DOS before and after ionization with Fe (+4 q_e).

Likewise, in the band structure there should be no change in the eigenvalue character, but because the Fermi level has shifted the occupancy is different, as seen in Fig. 25. Thus the expectation is the material should exhibit metallic properties due to ion replacement by Fe at the nitrogen-centered sites. A new unit cell was constructed, using the same lattice constant and atomic coordinates as the experimental $Ni_4(CN)_8$, but with the nitrogen-centered nickels replaced by iron. The same computational parameters were

used as in the previous structure, including the same 8x8x2 k-point mesh, energy cut-off, and exchange-correlation functional GGA (PBE).



Fig. 25 Holes are formed as electrons move from the valence to the conduction band. E_f should shift down, leaving the top of valence band partially occupied.

The calculations were spin-polarized, allowing for orbital states and charge densities to be separated via spin direction of electrons. The same approach was used to relax the inter-atomic distances, yielding a new lattice constant, 9.77958Å. Fig. 26 shows a comparison between the original experimental nickel cyanide inter-atomic distances with those of the Fe-doped structure. As with undoped nickel cyanide the new N-Ni distance shortened by approximately the same amount, from 2.01Å to 1.883Å.

Ni_Fe_(CN) Bonding Type	Exp. Inter-atomic Distances (Å)	Theo. Inter-atomic Distances
Ni-C	1.870	1.831
C-N	1.150	1.176
N-Ni/N-Fe	2.010	1.882

Fig. 26 Comparison of original experimental inter-atomic distances with $Ni_2Fe_2(CN)_{8.}$

Due the partially filled d-orbital nature of Fe, we investigated the stability of different magnetic states of Fe-doped Nickel cyanides. It was also important to investigate the potential magnetic properties of the new material, so two additional conditions were added: a ferromagnetic (FM) case with an initial magnetic moment of the same direction applied to both iron atoms in the structure, and an antiferromagnetic (AFM) case where the two moments are in opposite directions³. The magnetic moments as applied to the Ni₂Fe₂(CN)₈ are seen in Fig. 27.

In the FM case there can be seen a significant difference from the behavior of $Ni_4(CN)_8$. For undoped nickel-cyanides there were no partially occupied states at the Fermi level, and a band gap of 1.5eV. But due to the ion replacement by Fe the occupied states cross the Fermi level in one of the spin states, meaning that this material cannot be categorized as a semiconductor/insulator.



Fig. 27 20-atom unit cell for $Ni_2Fe_2(CN)_8$, for both anti-ferromagnetic and ferromagnetic cases.

Analysis of the integrated DOS indicates that the "up" spin states comprise the larger or "majority" number of electrons, while the "down" spin states represent the "minority" or lesser number of electrons. Fig. 28 shows the total DOS in the region of E_{f} ,

with the localized states in the minority spin direction exaggerated to show where this overlap is present. In the majority spin, plotted "up", there are no states to be occupied anywhere near E_f . This is a condition known as half-metallicity, meaning that while one electron spin direction acts like a metal, the other does not. This kind of electronic behavior figures prominently in the field of spintronics.



Fig. 28 (A) DOS split into majority- (up) and minority (down) spins for the ferromagnetic-ordered Fe ion configuration. (B) Expanded view of the spin-resolved density of state near the Fermi energy, E_f.

Now the minority spin DOS is decomposed to its d-orbitals present in the region around the Fermi level, seen in Fig. 29. As the behavior of both Ni and Fe atoms was the same they are both plotted together. The orbital splitting chart reveals the d_{z^2} shifted up into the unoccupied conduction region, while d_{yz} and d_{xz} overlap E_f and contribute the metallic behavior.



Fig. 29 The decomposition of the FM minority-spin d-orbitals and orbital splitting.

This indicates that in the minority spin, the transition metal d-orbitals are the principal contributors to electron transport, with the inclusion of the iron ions shifting the material in this direction. The presence of d_{z^2} in the conduction region in spite of no axial ligands is puzzling, and perhaps the result of orbital hybrization at the N-Fe bonds having fewer electrons to work with than in pure nickel cyanide. It should be noted that the overlap of states past E_f is only ~0.1eV, which gives us a good guide as to the behavior of the eigenvalues in the energy bands in this region.

Now the band structure is calculated, using the same square planar BZ across the same critical points M, Γ , X, W, and Γ . The calculations were done from the charge densities as created in the self-consistent run, as the critical points do not provide a three-dimensional grid from which to create sensible eigenvalues⁸. Fig. 30 shows majority and minority spin band structure plots near E_f for the FM magnetization. Concentrating first on the minority spin, there are bands which cross the Fermi level, meaning that they are occupied in some places and not in others. As with the DOS, the band structure confirms

metallicity in this spin. To see which bands are partially occupied, Fig. 31 focuses on band indicies 50-54.



Fig. 30 Majority and minority spin-polarized band structures for FM, Ni₂Fe₂(CN)_{8.} E_f is 0eV.

Here band indices 51 and 52 are shown to cross the Fermi level, and a review of the eigenvalues for all k-points associated with these bands reveals that they are partially occupied. The band width of the partially occupied bands is ~0.4eV, which is fairly shallow, suggesting a large effective mass and limited electron transport, although judging from the energy levels it is clear that at Γ the bands are unoccupied.



Fig. 31 Band indicies crossing E_f in minority spin for FM Ni₂Fe₂(CN)₈ are 51 and 52, and are partially occupied.



Fig. 32 Contributions of the d-orbitals for Ni and Fe around E_{f} , FM case. The principal contributions are from d_{yz} and d_{xz} .

37

Band indices higher than 52 are unoccupied and reside in the conduction band region, facilitating transport.

Now, the individual contributions of the d-orbitals are examined within the minority spin band structure, as seen in Fig. 32. From the plot it can be seen that they contribute all of the bands near $E_{\rm f}$, with some occupied, partially occupied, and unoccupied in this vacinity. The d_{xy} orbital bands sit beneath the top of valence band, with its greatest band width at ~0.2eV. The d_{yz} and d_{xz} orbitals are themselves in the region crossing $E_{\rm f}$, with a the latter in the partially occupied bands. The bottom of the conduction band has a very thin band width, and its main contributor d_{z^2} , at ~0.6eV. The $d_{x^2-y^2}$ orbital again resides unoccupied up in the conduction band.

Now, the antiferromagnetic (AFM) case is considered. Again, the only difference in calculations between this and the FM case above is that AFM has opposing magnetic moments on its Fe atoms. The total and localized DOS are shown in Fig. 33. The first thing that can be seen from the distribution of states is that both spins are symmetric, meaning that there is no majority or minority spin.



Fig. 33 Total and expanded view of DOS for the antiferromagnetic case, $E_f = 0eV$.

Moreover, since the states cross E_f they are only partially occupied, suggesting that this material is a metal, which was the original expectation when the magnetic moments were introduced. This is in contrast to the FM case, which exhibited halfmetallicity. Fig. 34 shows the d-orbital breakdown of the Ni and Fe atoms to the DOS in one spin. Like the FM case the d_{yz} and d_{xz} orbitals are partially occupied along the Fermi level, with d_{xy} in the valence region and the others up in the conduction region. The band structure is plotted in Fig. 35, where E_f is adjusted to 0eV. As the energy bands are identical for both spins, there is no difference between majority and minority spins.



Fig. 34 DOS is broken down into d-orbital contributions.

From the band structure, it can also be seen that the band widths crossing E_f is a very shallow 0.4eV. There is again a very thin band or bands near 0.6eV, likely the bottom of conduction band and consistent with DOS.

Now, the eigenvalues themselves were examined to determine which band indices were partially occupied. In Fig. 36 these bands are isolated and plotted, revealing that band indices 54 and 55 cross the Fermi level. These bands are associated with d_{xz} and d_{yz} , respectively.



Fig. 35 Band structure of the AFM case.

In Fig. 37, the contributions of the d-orbitals from the Ni and Fe atoms are explored. Here, the d_{yz} and d_{xz} orbitals cross E_f , meaning these bands are partially occupied and contribute to the AFM metallic character. The bottom of conduction band is revealed to be from the d_{z^2} orbital, as predicted by DOS. And the d_{xy} sits occupied within the valence region, while $d_{x^2-y^2}$ is in the conduction band.



Fig. 36 Band indices 54 and 55 cross E_f and are partially occupied, contributing metallicity.



Fig. 37 The contribution of the Ni and Fe d-orbitals in the band structure for the AFM case.

The presence of the Fe ions contributes charges to the conduction band, making this structure a metal for both FM and AFM. The FM case yields the interesting and unexpected half-metallicity. Given this development, the question that needs to be asked is: which magnetic disposition is more stable, the ferro- or antiferromagnetic? If this material was set into a particular magnetic moment at room temperature, then heated, would it retain its characteristics? The self-consistent calculations of each were considered, and it was found that the free energy value for the FM case was - 160.79504eV while the AFM case was -160.75626eV. Since the FM energy value is lower, it is the more stable value. Converting this energy difference into a physically relevant value, the two numbers were subtracted and the difference multiplied by a conversion factor of 11604.5K/eV to get a temperature change of 450.02K. So not only does the FM case have the lower energy, it would take a considerable temperature change to cause the doped material to lose its half-metallicity and convert to antiferromagnetic.

CHAPTER V

OTHER TRANSITION METALS

In Ni₂Fe₂(CN)₈ we found a material that, due to its contribution of charges to the conduction band, had metallic properties, and in its ferromagnetic phase a potential halfmetal with spintronics applications. Naturally, there are other transition metals which could also serve as dopants for nickel cyanide. In Fig. 38 the electronic configurations of all transition metals along Period 4 of the periodic table are listed. The difference between each of these, at least electronically, is with a couple exceptions in their 3d-subshells. While the Fe-doped case was found to be more stable in its ferromagnetic configuration, it is possible that adding or subtracting charge from the conduction band could yield different behavior.

Element	Electron Configuration	# Electrons per Unit Cell
Tı	[Ar]3d ² 4s ²	100
V	[Ar]3d ³ 4s ²	102
Cr	[Ar] 3d ⁵ 4s ¹	104
Mn	[Ar]3d ⁵ 4s ²	106
Fe	[Ar]3d ⁶ 4s ²	108
Co	[Ar]3d ⁷ 4s ²	110
Ni	[Ar]3d ⁸ 4s ²	112
Cu	[Ar]3d ¹⁰ 4s ¹	114
Zn	[Ar]3d ¹⁰ 4s ²	116

Fig. 38 The electronic configurations of transition metal elements along Period 4 of the periodic table, along with total # of electrons for each new 20-atom unit cell.

All of the above transition metal atoms were placed in new unit cells at the same nitrogen-centered sites as the Fe example. For each, new inter-atomic distances were found via relaxation of the lattice using the same CG method. Then, separate self-consistent calculations were performed using the new geometries and obeying the same constraints as in the previous structures. This was done for both ferromagnetic (FM) and antiferromagnetic (AFM) cases, again with the magnetic moments applied to the nitrogen-centered transition metal ions. The difference in the ground-state energies and corresponding temperatures for FM and AFM can be seen in Fig. 39. This chart also includes final calculated magnetic moment values for the two cases. From this chart we can see that, depending on the transition metal, the stability can change from FM to AFM.

Element	$\Delta E \rightarrow AFM-FM$ (meV)	ΔТ(К)	Mag. Moment: FM	Mag. Moment: AFM(±)
Ti	-59.36	688.84	1.523	1.493
V	72.14	837.15	2.412	2.432
Cr	-10.30	119.53	3.396	3.392
Mn	38.16	442.83	2.712	2.684
Fe	38.78	450.02	1.838	1.828
Co	-0.04	0.46	0.947	0.947
Ni	0.00	0.00	0.000	0.000
Cu	-6.84	79.38	0.617	0.612
Zn	0.00	0.00	0.000	0.000

Fig. 39 Chart of relative stabilities of transition metals along Period 4. The last two columns list calculated magnetic moments for FM and AFM configurations.

Fig. 40 is a graphical representation of this. From Ti to Fe, these shifts tend to be more dramatic with increasing population of the 3d-subshell, whereas after Fe they become almost negligible, with Zinc-doped non-magnetic due to its filled orbitals in 3d.



Fig. 40 Plots of (A) the relative energy stabilities of transition metal cyanides, and (B) their corresponding temperature differences.

The above chart also includes the calculated magnetic moments for each case. For each atom type, a theoretical magnetic moment can be found by just counting the number of valences in the unfilled 3d-subshell, with a value of ½ assigned to each spinpolarized electron. This gives us a number with which to compare with the actual magnetic moment that is found in FM and AFM cases, as seen below in Fig. 41.



Fig. 41 Comparison of FM and AFM magnetic moments with expected valences.

Manganese-doped Nickel Cyanide:

Manganese (Mn) is also along Period 4, in Group 7B of the periodic table. It has one less electron than Fe in its 3d-subshell, giving 106 electrons in the 20-atom unit cell. Fig. 42 shows the 3d-subshell splitting for Mn, with none of the orbitals having a pair of electrons. While Fe-doping contributed +2 q_e per atom to the conduction band, the Mndoped structure will yield +3 q_e per dopant atom, giving a total positive charge of +6 q_e . The expectation is that this will increase the metallicity of the Mn-doped structure.

Manganese: [Ar] $3d^{5}4s^{2}$

d _{xy}	d _{yz}	d _{xz}	d_2 ²	d _{x²-y²}
4	4	4	4	4

Fig. 42 3d-subshell orbitals for Manganese.

The 20 atom unit cell was again subjected to relaxation of its interatomic distances, and a final minimum energy lattice constant was found to be 9.862Å, as seen in Fig. 43. Whereas previously the relaxation of atomic distances resulted in nearly identical nitrogen-transition metal lengths, the Mn-doped case shows a value much closer to the experimental lattice values. For the production calculations we used the same criteria and k-point mesh as the other structures, with spin-polarization to discern orbital behavior.

Separate cases were again established for FM and AFM ordering of magnetic moments on the Mn atoms. Fig. 45 shows the FM density of states in the range of $\pm 3 \text{ eV}$, with all states shifted to the Fermi level, E_f. Evaluating the integrated DOS, the "up" spin

data is found to be the majority spin, while the "down" orientation is revealed as the minority spin.

$Ni_2Mn_2(CN)_8$ Bonding Type	Exp. Inter-atomic Distances (Å)	Theo. Inter-atomic (Å) Distances
Ni-C	1.870	1.836
C-N	1.150	1.174
N-Ni/ N-Mn	2.010	1.922

Fig. 43 Comparison of inter-atomic distances, original $Ni_4(CN)_8$ vs. $Ni_2Mn_2(CN)_8$.

This is behavior consistent with the Fe-doped structure. From the exaggerated DOS in Fig. 44(B), the minority states near E_f are clearly seen to be crossing the Fermi level and hence only partially occupied.



Fig. 44 (A) DOS split into majority- (up) and minority (down) spins for the ferromagnetic-ordered Mn-doped structure, and **(B)** expanded view of the spin-resolved density of state near the Fermi energy, E_f.

Presuming that the transition metal d-orbitals at the coordinate complex centers are again responsible for electron transport, the minority spin component d states near E_f are plotted in Fig. 45. It can be seen that while d_{xy} and d_{xz} orbitals are partially occupied as in the Fe-doped case, the d_{yz} orbital now resides in the conduction region with the d_{z^2} and $d_{x^2-y^2}$ orbitals. Like the Fe-doped structure, this distribution of states is consistent with half-metallic behavior.



Fig. 45 d-orbital splitting at the Fermi level for Ni₂Mn₂(CN)₈, FM case, minority spin.

The band structure for the FM case was now plotted, again differentiating by majority and minority spins. Fig. 46 shows the FM band structure resolved into its majority and minority spins. As with the DOS, the minority spin has bands which cross the Fermi level, while the majority spin has a considerable band gap of 2.4eV. This is again consistent with the half-metallic behavior seen in the Fe-doped case. A review of the band indices associated with the eigenvalues placed bands 50-52 as cutting across E_f and hence partially occupied.



Fig. 46 The spin-resolved FM band structures for the majority and minority spins of Mn-doped nickel cyanide.

Fig. 47 focuses on these bands, again showing that that band 50 in particular is nearly occupied with just a few unoccupied eigenvalues concentrated around the Γ point in the BZ.



Fig. 47 A close-up of Mn-doped minority spin FM band structure near E_f, showing partially occupied band indices.

Now the minority spin energy bands were evaluated for their transition metal dorbital content, and the result is seen in Fig. 48. Consistent with the DOS the d_{xy} orbital, associated with band index 50, is partially occupied and crossing the Fermi level the d_{xy} and d_{xz} orbitals making only a very marginal contribution around M (0.5, 0.5, 0.0).



Fig. 48 Illustration of minority spin d-orbital contributions near E_{f} .

Now the AFM case is considered. Fig. 49 shows the total DOS evaluated in the region \pm 4eV, along with all of the localized states near E_f. For the total DOS, it was found that this configuration is in fact a very narrow-band semiconductor, with a band gap of 0.26eV.



Fig. 49 The Mn-doped AFM DOS both (A) for \pm 4eV, and (B) a more localized expanded view near E_{f} .

This is in contrast to the Fe-doped case, whose AFM behavior was metallic. In Fig. 50 the d-orbital behavior is examined, revealing that unlike the FM case only the d_{xy} lying in the valence region, with the rest up in the conduction band.



Fig. 50 The AFM d-orbital splitting behavior for Ni₂Mn₂(CN)_{8.}

The AFM band structure is illustrated in Fig. 51, evaluated in the energy range - 1.6eV to 1.8eV. From the figure's expanded plot in Fig. 51(B), there are no energy bands which are partially occupied, making this a semiconductor with a band gap 0.26eV.



Fig. 51 (A) Mn-doped AFM band structure, and (B) expanded band indices near zero energy.

In Fig. 52, the contributions of the split d-orbitals are shown near zero energy. As with the DOS, only the d_{xy} orbital sits at the top of the valence band. The rest of the orbitals for the transition metal ions are up in the conduction band, although the band gap is again extremely narrow. Given the metallicity present in both FM and AFM Fe-doped cases the expectation was that both Mn-doped forms would show an even greater predisposition to metallic behavior. Although the difference the calculated magnetic moment for this structure and its iron-infused cousin was proportional to the expected valences for each, the AFM case for Mn is nonetheless non-metallic.



Fig. 52 Illustration of AFM band structure d-orbital contributions near zero energy.

53

Titanium-doped Nickel Cyanide:

Titanium (Ti) is the first of the transition metals along Period 4 which we studied. In our 20-atom unit cell, the use of Ti at the nitrogen-centered sites will result in a total electron count of 100. From the energy stability evaluation we found that Ti-doped nickel cyanide was partial to its antiferromagnetic phase and had the largest temperature differential of any of the dopants, -688.84K. In contrast to Fe and Mn, this atom type has almost completely empty orbitals in its 3d-subshell. Each Ti ion has an extra +8 q_e to contribute to the conduction band, giving a total of +16 q_e . The valence shown in Fig. 53 for this element shows only two electrons in the d_{xy} and d_{yz} orbitals, both with the same spin.

d _{xy}	d _{yz}	d _{xz}	d _z ²	$d_{x^2 - y^2}$
4	4			

Fig. 53 The electron configuration and d-orbitals filled for Ti.

For the FM case, the lattice constant found from relaxation of inter-atomic distances was 10.18Å, somewhat larger than the experimental lattice constant.

A comparison chart is seen in Fig. 54, where there is a significant increase in the inter-atomic distance for the nitrogen-centered sites where the Ti atoms have been substituted, from 2.01Å to 2.085Å. The self-consistent calculation was performed, and the integrated DOS revealed that the "up" spin was the majority, while "down" was the minority spin. The total and localized DOS are seen in Fig. 55.

In the exaggerated plot in Fig. 55(B) there can be seen in the spin-resolved upper panel a band gap of 0.15eV, showing that this structure with this magnetic disposition is a semiconductor.

Ni Ti (CN) ₈ Bonding Type	Exp. Inter-atomic Distances (Å)	Theo. Inter-atomic Distances (Å)
Ni-C	1.870	1.829
C-N	1.150	1.177
N-Ni / N-Ti	2.010	2.085

Fig. 54 The comparison of inter-atomic distances for the experimental and Ti-doped lattice constants.

Since Ti has a significantly smaller expected and calculated magnetic moment than that of either Fe or Mn, the expectation would be that this is material would be less or non-magnetic, confirmed by this result.



Fig. 55 In (A) the total DOS and (B) expanded view of DOS for Ni₂Ti₂(CN)₈, spinresolved FM case.

Fig. 56 shows the d-orbital splitting of the majority spin states lying in the region near the Fermi level. This split shows the d_{yz} and d_{xz} orbitals for this spin contributing in the valence region while the rest of the orbitals reside up in the conduction band. This is curious in that the d_{xy} orbital, so far the consistently lowest in energy in the other structures, is now also unoccupied.



Fig. 56 The d-orbital splitting for the majority spin FM DOS.

Another point of interest is that where the Fe- and Mn-doped structures contained states near E_f in the minority spin, here this behavior is seen in the majority spin. Next the band structure is considered, illustrated in Fig. 57. The energy bands are again spin-resolved into majority and minority, and shifted to zero energy. As in the DOS, the majority spin shows a very thin band gap of 0.15eV, and the minority spin has no eigenvalues near zero energy. Next the band structure is considered, illustrated in Fig. 58. The energy bands are again spin-resolved into majority, and shifted to zero energy.



Fig. 57 The spin-resolved FM Ti-doped band structures for the majority and minority spins.

As in the DOS, the majority spin shows a very thin band gap of 0.15eV and the minority spin has no eigenvalues near E_f . The band indices around the Fermi level were confirmed to be either fully occupied or unoccupied, as seen in Fig. 58.



Fig. 58 A close-up of the Ti-doped minority spin FM bands near zero energy, which shows no partially occupied bands.

The AFM self-consistent calculation yielded the total and localized density of states as seen in Fig. 59. As in the Mn-doped case, this structure has a band gap of 0.26eV and therefore exhibits semiconductor behavior. The majority spin d-orbital split is shown in Fig. 60.



Fig. 59 The **(A)** total DOS and **(B)** expanded view of DOS for Ni₂Ti₂(CN)₈, spin-resolved AFM case.

The spin-resolved band structure is shown in Fig. 61, again shifted to zero energy and with the same band gap of 0.26eV.



Fig. 60 The d-orbital splitting for the majority spin AFM DOS.

The results for $Ni_2Ti_2(CN)_8$ show a material that is a magnetic semiconductor regardless of the orientation of the magnetic moments on the nitrogen-centered transition metal ions.



Fig. 61 (A) The AFM Ti-doped band structure, and (B) bands close to zero energy.

CHAPTER VI

SUMMARY

Using density functional theory with spin-resolved local density approximations (LSDA), we investigated the electronic structure properties of monolayer nickel cyanide $(Ni_4(CN)_8)$ and its transition metal-doped variants. Working from experimental data and a 20-atom unit cell we relaxed the inter-atomic distances to find a minimum lattice constant for the structure of 9.6865Å. One interesting result was the shortening of the N-Ni distance from the experimental values so that it was nearly equal in length with that of the Ni-C distance.

Then the density of states (DOS) for this new structure was calculated, showing that Ni₄(CN)₈ is a narrow-band semiconductor with a band gap of 1.4eV. Splitting the DOS into its component s, p, and d orbital contributions revealed the dominant presence of d at the Fermi level (E_f), which could only come from the Ni atoms. Then the d states were decomposed into their respective orbitals. Since the structure is square planar the d_{xy} has the lowest as it has no direct repulsion from the CN- ligands. The d_{z^2} orbital is next, having only a small, localized relationship with the x-y axes. The d_{yz} and d_{xz} are degenerate, and the $d_{x^2-y^2}$ has the highest energy, being the only orbital directly residing along the xy-axes, which face direct repulsion from the ligands. These results all confirm expected behavior via ligand field theory. The band structure confirmed this result. Analyzing the eigenvalues in k-space along the edges of the square planar Brillouin zone (BZ), the plot showed a semiconductor with a band gap of 1.7eV.

Next, we attempted to replicate the results of the experiment⁴ by replacing nitrogen-centered Ni atoms with Fe atoms. Electronically, we expected this material to be a non-magnetic metal due to the $+2 q_e$ charge contributed to the conduction band from each Fe ion added to the unit cell. However, since this is a new material we took into account the possibility of magnetic behavior by applying to the Fe atoms both a ferromagnetic (FM, magnetic moments in the same direction) and antiferromagnetic (AFM, moments in opposite directions). The inter-atomic distances were relaxed, and once again the N-Fe length shortened to nearly the same as the Ni-C.

For the Analysis of the DOS revealed a surprising result: the spin-resolved minority states were metallic in nature, while the majority spin was insulating. This halfmetallicity showed a new d-orbital splitting regime, apparently due to the presence of the Fe atoms. In the FM minority spin, d_{z^2} has now increased in energy and is in the conduction region. The d_{xy} and $d_{x^2-y^2}$ orbitals are in the valence and conduction regions respectively, while the d_{xy} and d_{xz} are partially occupied and responsible for the metallicity. Again, the band structure confirmed this. In AFM, the DOS result was a metal. Here, the d-orbital splitting is the same as the FM variant but the forced orientation of the magnetic moments causes both spins to become metallic. Calculating the energy difference between the two orientations revealed that FM was the more stable, which would suggest its use as a monolayer with spintronics applications. This result led to the decision to explore other transition metal dopants at the same nitrogen-centered sites in the structure, exploring both FM and AFM magnetic orientations. It was shown that DFT was able to reasonably replicate the magnetization of all the materials studied, compared with the calculated valence of the transition metal atoms. When the relative stabilities were calculated, we decided to consider two other cases of each type: Manganese (Mn) for FM and Titanium (Ti) for AFM. For Mn, the FM case was found in DOS to be a half-metal but curiously the AFM orientation was a semiconductor with a band gap of 0.26eV. In the case of Ti, both the FM and AFM cases are semiconductors, with band gaps of 0.15eV and 0.26eV respectively.

In conclusion, $Ni_4(CN)_8$ can be doped with different transition metal atoms to create different monolayer materials ranging from thin-gapped semiconductors to metals to half-metals. Future work on this material would involve examining two or more layers of the material, to see what electronic structure effects might be present.
BIBLIOGRAPHY

¹ "Chemistry: The Molecular Science", John W. Moore, Conrad L. Stanitski & Peter C. Jurs, Brooks/Cole (Thompson Learning), ISBN: 0-03-032011-9. (1)

² "Inorganic Chemistry: An Industrial and Environmental Perspective", TW Swaddle, Academic Press, ISBN: 0-12-678550-3.

³ "Inorganic Structural Chemistry", 2nd Edition, Ulrich Müller, John Wiley & Sons, Ltd., ISBN-10: 0-470-01864-X (HBK), 0-470-018650-8 (PBK).

⁴ "Investigation of Metal Cyanides using X-Ray Diffraction & Thermal Gravimetric Analysis", Kerrylynne Pattie, Southwestern University (2010).

⁵ "A Bird's Eye View of Density Functional Theory", Klaus Capelle, Univ. of São Paulo Dept. of Physics, (2006).

⁶ "GGA Made Simple", John P. Perdew, Kieron Burke & Matthias Ernzerhof, Phys. Rev. Letters 77, #18 (1996).

⁷ "Introduction to Solid State Physics", 5th Edition, Charles Kittel, John Wiley & Sons, Inc., ISBN: 0-471-49024-5.

⁸ "VASP the Guide", G. Kresse & J. Furthmüller, Inst. for Material Physics, Univ. of Vienna, 2007.

⁹ "Efficient Iterative Schemes for Ab Initio Total-Energy Calculations using a Planewave Basis Set", G. Kresse & J. Furthmüller, Phys. Rev. B 54 (1996), DOI: 10.1103/PhysRevB.54.11169.

¹⁰ "Semiconducting Cyanide-Transition Metal Nanotubes", Yina Mo and Effhimios Kaxiras, Small 3 (2007), DOI: 10.1002/smll.200700033.

¹¹ "Surprises from a Simple Material – The Structure and Properties of Nickel Cyanide", Simon Hibble, Ann M. Chippindale, Alexander Pohl & Alex C. Hannon, Angew. Chem. Int. Ed. 46 (2007), DOI: 10.1002/anie.200701246.

VITA

Craig Higgins was born March 25th, 1969, in New Orleans, La. He graduated from De La Salle High School in New Orleans in 1987. He achieved his Bachelor's in Science in Geophysics in 1996, and his Master's in Applied Physics in 1998, both from the University of New Orleans. He joins Texas Tech University's physics department as a Ph.D candidate in the Fall, 2010.

Permanent Address: 1707 Aquarena Springs Dr. #214 San Marcos, Tx. 78666

This thesis was typed by: Craig Higgins