SIZE AND NITROGEN CATALYTIC EFFECTS ON
THE MAGNETIC PROPERTIES OF FE THIN FILMS

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Summary

The effects of physical size reduction and catalytic nitridation on the ferromagnetic behavior of Fe films were investigated using three approaches: (i) a theoretical study was conducted that involved incorporating the bond-order-length-strength (BOLS) and bond-band-barrier (BBB) correlations [C. Q. Sun, Prog. Mater. Sci. 48(6), 521 (2003)] in the Ising model premise and Brillouin functions to predict the magnetic performance at different temperatures; (ii) Monte Carlo simulations were carried out on the spin system with various cluster sizes and geometric shapes to verify the BOLS predictions; and (iii) nickel, iron, and iron nitride films were deposited using the filtered cathodic vacuum arc technique and were characterized to confirm the predictions and Monte Carlo simulations.

It was found that when a solid (particle or film) forms at a nanometer scale, the effect of atomic coordination number (CN) imperfection and the following effect on the bond-length-strength dominate, which localize the charges that contribute to the angular momentum ($J$) and hence the magnetic moment ($\mu$) of the system. The CN imperfection also affects the atomic cohesion, or the spin-spin exchange interaction, of the lower-coordinated atoms, which determine the phase stability, or Curie temperature ($T_C$) suppression. The competition between charge localization and atomic cohesive energy reduction determines the magnetic behavior of a nanosolid at various temperatures. The coercivity ($H_C$), however, increases with the increase of size due to the rise of intergrain interaction. Understanding of the size-induced phase stability was extended to
the ferroelectric and superconductive nanosolid with consideration of the high-order exchange interaction.

It was also found that nitrogen addition affects the $\mu$ of an iron atom by changing its valence states from Fe to Fe$^{\text{dipole}}$, which possesses higher $J$ and hence $\mu$ compared with pure Fe. A small amount (~10 at%) of nitrogen in the iron films enhances the $M_S$, which can be even larger than the value of bulk iron, while excess nitrogen decreases the $M_S$. The excess nitrogen-lowered $M_S$ was attributed to the reduction of Fe$^{\text{dipole}}$ due to the polarized electron’s being captured by the excess nitrogen atom.

Consistency between theory predictions and the simulative/experimental results shows that the saturation magnetization $M_S$ and $T_C$ relate to spin-spin exchange energy or the cohesive energy, while the $H_C$ relates to the intergrain exchange energy. The $M_S$ also relates to the $\mu$ of individual atoms, which is affected both by the charge localization due to bond contraction and by nitrogen addition that alters the valence value of the Fe atoms. The findings should find applications in designing nanomagnetic devices such as magnetic sensors and magnetic storage media. The study may allow us a more feasible mechanism for adjusting the magnetic behavior of the films by means of both the physical shape and size, and the chemical reaction.
# Table of Contents

ACKNOWLEDGMENTS ........................................................................................................... I  
SUMMARY ......................................................................................................................... IV  
TABLE OF CONTENTS ........................................................................................................ VI  
LIST OF FIGURES ................................................................................................................ VIII  
LIST OF TABLES .................................................................................................................. XII  
ABBREVIATIONS ................................................................................................................ XIII  

CHAPTER 1 INTRODUCTION ........................................................................................................ 1  
1.1 MOTIVATION ................................................................................................................... 1  
1.2 OBJECTIVES ................................................................................................................... 4  
1.3 MAJOR CONTRIBUTIONS ............................................................................................... 5  
1.4 ORGANIZATION .............................................................................................................. 7  

CHAPTER 2 LITERATURE SURVEY .......................................................................................... 10  
2.1 PHYSICAL SIZE EFFECT ............................................................................................... 10  
\hspace{1em} 2.1.1 \textit{M} \textit{S} suppression or elevation ........................................................................ 10  
\hspace{1em} 2.1.2 \textit{T} \textit{C} suppression ............................................................................................. 17  
\hspace{1em} 2.1.3 \textit{H} \textit{C} and \textit{\mu}_p ................................................................................................. 19  
2.2 NITRIDATION EFFECT .................................................................................................. 21  
\hspace{1em} 2.2.1 Iron-nitrogen system ....................................................................................... 21  
\hspace{1em} 2.2.2 Synthesis of nitride films .................................................................................. 25  

CHAPTER 3 APPROACHES ...................................................................................................... 29  
3.1 THEORY .......................................................................................................................... 29  
\hspace{1em} 3.1.1 BOLS correlation ............................................................................................. 29  
\hspace{1em} 3.1.2 BBB correlation ............................................................................................... 33  
\hspace{1em} 3.1.3 Ising model – exchange interaction ................................................................ 33  
3.2 MONTE CARLO SIMULATION ..................................................................................... 34  
\hspace{1em} 3.2.1 Introduction ......................................................................................................... 34  
\hspace{1em} 3.2.2 Methodology ...................................................................................................... 35  
\hspace{1em} 3.2.3 The algorithm of Metropolis ............................................................................. 37  
\hspace{1em} 3.2.4 Spin system ......................................................................................................... 38  
3.3 EXPERIMENTAL DETAILS .......................................................................................... 41  
\hspace{1em} 3.3.1 Filtered Cathodic Vacuum Arc (FCVA) system .............................................. 41  
\hspace{1em} 3.3.2 Shield for magnetic target ............................................................................... 44  
\hspace{1em} 3.3.3 Sample preparation ............................................................................................ 46  
\hspace{1em} 3.3.4 Characterization methods ................................................................................. 49  

CHAPTER 4 RESULTS AND DISCUSSION I: PHYSICAL SIZE EFFECTS ....................... 52  
4.1 BOLS PREDICTION ........................................................................................................ 52  
\hspace{1em} 4.1.1 \textit{M} \textit{S} variation ................................................................................................. 52  
\hspace{1em} 4.1.2 \textit{T} \textit{C} suppression ............................................................................................... 59  
4.2 MONTE CARLO SIMULATION .................................................................................... 64  
\hspace{1em} 4.2.1 \textit{M} \textit{S}(K, T) enhancement at Low \textit{T} .................................................................... 65
Table of Contents

4.2.2 \( M_S(K_\text{r}, T) \) tailoring at mid-\( T \) ....................................................... 65  
4.2.3 \( M_S(K_\text{r}) \) oscillation and structural stability ........................................ 70  
4.2.4 \( T_C \) suppression ........................................................................... 73  
4.3 EXPERIMENTAL VERIFICATION........................................................................ 74  

CHAPTER 5 RESULTS AND DISCUSSION II: NITROGEN-CATALYTIC EFFECT ........................................................................ 82  
5.1 BBB PERDITION .................................................................................. 82  
5.1.1 \( M_S \) ............................................................................................... 82  
5.1.2 Resistivity ................................................................................... 85  
5.2 DEPOSITION OF Fe-N FILMS ................................................................. 86  
5.2.1 Deposition rate ........................................................................... 87  
5.2.2 Surface morphology ................................................................... 88  
5.2.3 Microstructure ........................................................................... 89  
5.2.4 Binding energy ........................................................................... 89  
5.3 NITROGEN CATALYTIC EFFECT ............................................................ 92  
5.3.1 \( M_S \) ............................................................................................... 92  
5.3.2 Coercivity and squareness ......................................................... 95  
5.3.3 Resistivity ................................................................................... 95  
5.4 EXTENSION: BIAS EFFECT .................................................................... 97  
5.4.1 Deposition rate and surface morphology .................................. 98  
5.4.2 Microstructure ......................................................................... 100  
5.4.3 Magnetic properties ................................................................. 101  
5.4.4 Discussion ................................................................................ 101  

CHAPTER 6 RESULTS AND DISCUSSION III: JOINT EFFECT OF PHYSICAL SIZE AND NITRODATION ON \( M_S \) ....................................................... 105  
6.1 NITROGEN-POOR Fe-N FILMS ............................................................ 105  
6.2 NITROGEN-RICH Fe-N FILMS ............................................................. 107  

CHAPTER 7 APPLICATION OF BOLS: \( T_C \) SUPPRESSION OF FERROELECTRIC AND SUPERCONDUCTING NANOSOLIDS111  

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS .......... ........... 119  
8.1 CONCLUSIONS ................................................................................... 119  
8.2 RECOMMENDATIONS FOR FURTHER RESEARCH ............................. 122  

LIST OF PUBLICATIONS ............................................................................. 123  
BIBLIOGRAPHY ............................................................................................ 125  
APPENDIX I .................................................................................................. 144  
APPENDIX II .................................................................................................. 155
List of Figures

Figure 2.1 The average magnetic moment per Co atom and the percentage of magnetic Co atoms as a function of the cluster size. .......................... 11

Figure 2.2 Magnetic moments of Ni$_n$ particles as a function of size, at temperatures between 73 and 198 K. ............................................ 12

Figure 2.3 Deviation from the bulk magnetic moment in (a) Fe, (b) Co, and (c) Ni as a function of nearest neighbor coordination (in various structures). .......................................................... 14

Figure 2.4 Phase diagram of the Fe-N system. .................................. 21

Figure 2.5 A schematic illustration of the crystal structure of (a) $\alpha$-Fe; (b) $\alpha''$-Fe$_{16}$N$_2$; (c) $\gamma$-Fe$_4$N; (d) FeN with ZnS structure; and (e) FeN with NaCl structure. .......................................................... 24

Figure 3.1 Schematic illustration of the effect of atomic CN imperfection on the bond length and atomic trapping potential well depth of the lower-coordinated atoms near the edge of a surface. The deepened atomic potential ($V_{\text{atom}}$) confines electrons that contribute to the magnetic momentum of the lower-CN atoms. $\delta_{\text{surf}}$ is the perturbation to the crystal potential ($V_{\text{crystal}}$) due to CN imperfection. ......................................................... 31

Figure 3.2 CN dependence of bond contraction derived from Goldschmidt’s premise, and findings of Feibelman (open square) in which CN = 12 is the standard. ................................................................. 32

Figure 3.3 Example structure of fcc dot. The red atoms belong to the first out shell. The atoms in the first out layer of N$_{141}$ are much fewer in number than those of particle N$_{135}$, indicating the oscillations of the surface state when a particle is growing up. ...................... 38

Figure 3.4 Fcc rod and fcc plate spin system............................................ 40

Figure 3.5 The illustration of (a) Icosahedron N$_{147}$, (b) Marks decahedron N$_{101}$, and (c) fcc truncated octahedron N$_{201}$. ........................................... 40

Figure 3.6 The FCVA system with two six-inch diameter OPDB filters (R&D) .................................................................................. 42

Figure 3.7 Schematic illustration of the FCVA system.............................. 42

Figure 3.8 Schematic illustration of the modified cathode for the magnetic target. The cathode consists of the target and its supporter with a water-cooling system. The shield consists of three main parts: the aluminum cylinder, the pure iron O-ring, and the BN O-ring. .... 44

Figure 3.9 Magnetic targets (a) with and (b) without using the designed shield. ................................................................................. 45

Figure 3.10 The three approaches introducing nitrogen gas: (I) nitrogen is introduced directly into the chamber; (II) nitrogen is introduced into the plasma region near the target; and (III) nitrogen is introduced into the linear ion beam source. ........................................... 48
Figure 4.1 Counter plot of the BOLS predicted (see Eq (4.8)) $M_S(T, K_j)$ for dot/particle, which shows that the $M_S$ increases inversely with size at low temperature and decreases with size at mid-temperature. The $M_S$ is normalized by $M_S(T = 0, K_j = \infty)$ and $T$ is normalized by $AE_{exc}(\infty)$.

Figure 4.2 The typical pair-wise potential for interatomic interaction. The BOLS correlation mechanism indicates that the bond length decreases with the CN of an atom at the surface with a response of a bond energy rise (in absolute value). The $E(T_C)$ corresponds to the total energy at $T_C$. The separation between $E_b = 0$ and $E(T_C)$ is constant for all the bonds for a specific material and the separation between $E_b(d)$ at the equilibrium atomic distance and $E(T_C)$ is the thermal energy required to disorder the spin-spin interaction.

Figure 4.3 Comparison of the predicted $T_C$ suppression (solid, dash and dot line) with observations (sporadic symbol) of (a) Ni thin films: data 1, data 2, 3, 4, data 5, data 6, and data 7; (b) Co films; and (c) Fe films.

Figure 4.4 Comparison of the predicted (solid and dash line) and the measured $T_C$ suppression of Fe$_3$O$_4$ nanoparticle (square symbol).

Figure 4.5 MC-simulated temperature and size dependence of the $M_S$ for (a) fcc dot, (b) fcc rod, (c) fcc plate, and (d) Icosahedral spin systems.

Figure 4.6 The two outstanding regions showing the size-dependent $M_S(K_j, T)$ derived by MC simulation: (a) $k_BT/J_{exc} = 1$ (low-T); (b) $k_BT/J_{exc} = 6$ (mid-T) $|M_l|$ shift = $[|M_l(K_j)|-|M_l(\infty)|] / |M_l(\infty)| \times 100\%$.

Figure 4.7 Comparison of the size dependence of the $M_S$ of the fcc spherical particle, icosahedra, Marks decahedron (labeled as decahedron in the figure) and fcc truncated octahedron (labeled as octahedron in the figure) at temperature (a) $k_BT/J_{exc} = 1$ and (b) $k_BT/J_{exc} = 6$, showing the oscillation features and the structural stability. Lower $M_S$ at low T indicates that fewer atoms are located at the surface, corresponding to a more stable structure.

Figure 4.8 Shows the quantized S/V ratio $\gamma$ of the first surface layer of fcc and bcc structures.

Figure 4.9 The size dependence of $T_C$ shift by MC simulation together with the BOLS prediction.

Figure 4.10 The typical surface morphology of Ni thin film deposited on silicon substrate using FCVA. The surface is smooth with a roughness (RMS) of about 0.8 nm.

Figure 4.11 X-ray diffraction pattern of the Ni film at various substrate temperatures. The peak intensity decreases and the peaks become broader with the decrease of the substrate temperature, indicating a decrease in crystalline size.
Figure 4.12 Size dependence of the M-H loops of Ni films. .................................................. 77
Figure 4.13 Crystalline size dependence of $M_s$ under the maximum applied of 10 k Oe at ambient. The tendency agrees with most of the experiment observations and the Monte Carlo calculations in region II. The solid line and dot line are the theoretical prediction based on Eq. (4.18) with $\alpha(T) = 4.0$ and lower temperature $\alpha(T) = 1.6$ respectively. .................................................. 77
Figure 4.14 Size-enhanced $H_C$ characterized at room temperature. .................. 79
Figure 4.15 The squareness factor and remanence ratio as a function of size... 80
Figure 4.16 M-H loops of Ni films 148 nm thick under field applied to the direction parallel (//) and perpendicular (⊥) of the surface plane.... 81
Figure 5.1 The BBB model for nitridation. N hybridizes and interacts with arbitrary element B through the bonding and nonbonding lone pair to form the quasitetrahedron: NB₃ [N⁻³ + 3B⁺¹ (labeled 1) + B (dipole, labeled 2)]. The number and orientation of the lone pair give different geometrical symmetry as indicated. .......................... 83
Figure 5.2 Possible distribution of 3d and 4s electrons of Fe, Fe⁺, Fe⁺², and the dipoles. ................................................................. 84
Figure 5.3 The deposition rate R varies (a) with $P_N$ in approach II and (b) $P_N:P_{Ar}$ in approach III. ................................................................. 87
Figure 5.4 Typical AFM surface morphology of the Fe-N films deposited using approaches II and III. With an RMS value of about 0.3 nm, the films using approach II are far smoother than those with an RMS about 1.6 nm deposited using approach III. The films thickness is 75 ± 5 nm................................................................. 88
Figure 5.5 XRD profiles of the Fe-N films. (a) II-1 ($P_N = 2.0 \times 10^{-4}$ torr) & II-4 ($P_N = 0.7 \times 10^{-4}$ torr) show nitrogen-poor phases. (b) III-1 ($P_N:P_{Ar} = 100:7$) exhibits $\gamma''$-FeN phase. (c) II-2 ($P_N:P_{Ar} = 80:7$) presents $\delta$ and $\gamma'$ phases. (d) III-3 ($P_N:P_{Ar} = 40:7$) and (e) III-4 ($P_N:P_{Ar} = 50:7$) show $\zeta$-Fe₂N phase. Only weak $\alpha$ and $\alpha'$ peaks can be observed in (f) III-6 and III-7 ($P_N:P_{Ar} = 20:7$ and 10:7 respectively). (films thickness: 75 ± 5 nm)................................................................. 90
Figure 5.6 XPS binding energy of Fe, III-1, III-4, III-6, and II-1. The intensity of peak 707 decreases while peak 711 increases, which indicates the number increase of Fe²⁺ and Fe³⁺. ................................................................. 91
Figure 5.7 XPS binding energy of N1s in samples III-1, III-4, III-6, and II-1. The increase of the intensity indicates the increase of nitrogen concentration........................................................................................................ 92
Figure 5.8 M-H loops of samples deposited with the gas introduction method of (a) I and II, and (b) III. (films thickness: 75 ± 5 nm) .... 93
Figure 5.9 The $4\pi M_s$ of the films with different nitrogen concentration. The $4\pi M_s$ of the nitrogen-poor films are higher than those of the pure Fe film, while the $4\pi M_s$ of the nitrogen-rich films are lower........... 94
List of Figures

Figure 5.10 The nitrogen concentration dependence of the $H_C$ of the Fe-N films. $H_C$ tends to decrease with oscillation behavior when nitrogen increases.............................................................. 96

Figure 5.11 The resistivity of the Fe-N films increases exponentially with the increase of nitrogen concentration, which indicates the reduction of carrier concentration of iron and the formation of a band gap by nitriding. The dash line comes from a linear fitting. ........................................... 97

Figure 5.12 AFM images of the films deposited at various bias voltages........ 99

Figure 5.13 Bias dependence of surface roughness (RMS). The film deposited at $-50$ V bias voltage exhibits the lowest RMS value. .... 99

Figure 5.14 Bias dependence of the XRD profiles shows that the film deposited at $-50$ V bias voltage exhibits the highest intensity, indicating the best crystallinity among the samples. .................. 100

Figure 5.15 (a) The magnetic hysteresis loops of films deposited at bias voltage of $-50$, $-100$, and $-400$ V respectively. (b) Bias voltage effect on the $4\pi M_S$ of the films ................................................. 102

Figure 6.1 XRD profiles of Fe-(N-Poor) films with poor nitrogen concentration deposited at various substrate temperatures........ 106

Figure 6.2 Substrate temperature $T_S$ dependence of grain size of the Fe-(N-Poor) films. .................................................................................................................. 106

Figure 6.3 The M-H loops of low-nitrogen content films. ...................... 107

Figure 6.4 XRD profiles of Fe-N films at various substrate temperatures. ..... 108

Figure 6.5 $T_S$ dependence of the grain size of Fe-(N-Rich) films. .......... 108

Figure 6.6 The M-H loops of Fe-(N-Rich) films of various grain sizes. ....... 109

Figure 6.7 Physical size and nitrogen catalytic effect on the magnetization of iron thin films............................................................... 110

Figure 7.1 Schematic illustration of (a) short-range exchange loss for ferromagnetic nanoparticle, where only the nearest neighbor is considered; and (b) high-order exchange bonds loss of an atom in a spherical nanosolid with radius $R = K_C d$. $K_C$ is the critical radius; the lost $V_{vac}$ (the shaded portion) is calculated by differencing the volumes of the two spherical caps:.......................... 114

Figure 7.2 $T_C$ suppression of (a) PbTiO$_3$, SrBi$_2$Ta$_2$O$_9$, BaTiO$_3$, and PbZrO$_3$ nanosolids; and (b) superconductive MgB$_2$-1, MgB$_2$-2, and Pb nanosolids. $K_C$ is the critical correlation radius. .................................................... 115

Figure 7.3 Critical correlation radius $K_C$ dependence of the $T_C$ shift of ferroelectric and superconductive alloying nanosolids. For the $K_C = 5$ example, the bond contraction lowers the $T_C$ by $-41.1\%$ and the high-order bond lost (Bond lost) contribution that is a constant lowers the $T_C$ by $-53\%$, and the overall $T_C$ shift is $-94\%$. $K_C \leq 4$, $T_C = 0$. .................................................. 117
List of Tables

Table 2.1 Discrepancy in the $M_S$ as a function of size................................. 16
Table 2.2 Survey of Fe-N magnetic films and powders. ................................. 26
Table 2.3 Magnetic moment of Fe/Fe-N.$^{141}$ ........................................ 27
Table 3.1 Magnetic nanoparticle systems for Monte Carlo simulation (R is the radius of the particle, $N_i$ is the atomic number of $i$th shell, $N_j$ is the atomic number of the whole particle, and $z_i$ is the CN of the atoms in the $i$th shell). ......................................................... 39
Table 3.2 Icosahedron, Marks decahedron, and fcc truncated octahedron particles used in MC simulation. ......................................................... 41
Table 3.3 Film deposited with various nitrogen concentrations...................... 47
Table 3.4 Deposition conditions of Fe-N films at various substrate temperatures................................................................. 49
Table 4.1 Size effect on the in plane magnetic properties of Ni films............... 81
Table 5.1 Variations of angular momentum of Fe with its atomic states.$^{152}$ .... 84
Table 5.2 Summary of the magnetic properties of Fe-N films.$^{178}$ ............... 96
Table 7.1 Summary of information on the bulk atomic diameter, $d$, $T_c(\infty)$, and the critical radius $K_C$ at which the central atom lost its ferroelectricity attenuates. $K_C \leq 4$ corresponds to $T_c = 0$. The critical radius $R'_C$ at which $T_c = 0$ is derived by other models.$^{90}$ .... 118
## ABBREVIATIONS

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<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>BBB</td>
<td>Bond-band-barrier</td>
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<tr>
<td>bcc</td>
<td>Body-centered cubic</td>
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<tr>
<td>BOLS</td>
<td>Bond-order-length-strength</td>
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<td>DOS</td>
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CHAPTER 1 INTRODUCTION

1.1 Motivation

Nanostructured magnetic materials have attracted a great deal of attention because of their potential applications in areas such as high-density magnetic data storage,\(^1\) magnetic sensors,\(^2,3\) color imaging,\(^4\) bioprocessing,\(^5\) and magnetic refrigeration,\(^6\) as well as their significance in fundamental understandings.\(^7,8\) Properties of very small metal particles have been extensively studied in the past 50 years,\(^9\) and much is known about their electronic and geometrical structure. The magnetic properties of nanosize particles differ from those of bulk in two aspects. One is that the large surface-to-volume ratio (\(S/V\) ratio) results in a different local environment for the surface atoms in their magnetic coupling/interaction with neighboring atoms, leading to the mixed volume and surface magnetic characteristics; the other is that, unlike bulk ferromagnetic materials, which usually form multiple magnetic domains, several small ferromagnetic particles could consist of only a single magnetic domain. In the case of a single particle being a single domain, superparamagnetism occurs.

There are several distinct phenomena for magnetic nanomaterials with the decrease in size; for example, the Curie temperature (\(T_C\)) drops with size.\(^10\) - \(^19\) The \(T_C\) suppression is a critical problem for magnetic material application in nanometer scales because it may cause structural failure with loss of the ferromagnetic properties. On the other hand, the tunable \(T_C\) would be an advantage for magnetic sensors or switches that can function in an expected temperature range. The saturation magnetization (\(M_S\)) also varies with decreasing size. There are two opposite trends of observation. One is that the
CHAPTER 1 Introduction

\( M_S \) decreases with size; \(^{20-23}\) the other, however, is that the \( M_S \) increases inversely with size. \(^{24-27}\)

Several models have been proposed to explain the size-induced \( T_C \) suppression, including the spin-spin correlation length (SSCL) limitation. \(^{28,29}\) More recently, Nikolaev and Shipilin \(^{30}\) proposed that the ferromagnetic \( T_C \) suppression results from the surface layer that contains atoms with only half the number of exchange bonds per unit volume compared with the bulk. However, the understanding of the underlying mechanism of \( T_C \) suppression is under debate. A number of theoretical models have been developed to explain the size-enhanced or tailored magnetization. However, discrepancy remains. A shell model, \(^{21}\) which calculates the average magnetic moment of the system by considering the different magnetic moments in the surface layers, suggested that the average \( M_S \) is enhanced, as the magnetic moment of the surface layer is higher than the bulk value. On the other hand, Monte Carlo simulation \(^{31}\) based on the Ising model showed that even at temperatures well below the \( T_C \) of the bulk, the \( M_S \) of the small clusters is lower than the bulk value. Hence, a consistent model is highly desirable to explain the size-induced \( T_C \) suppression and \( M_S \) tailoring/enhancement.

Introducing atoms of an electronegative element and/or changing the distances of the interacting moments can be realized in the iron-nitrogen (Fe-N) system. The magnetic properties of the nitrogen-poor phases from this system are of interest from the magnetic point of view; \(^{32}\) for example, the \( \gamma' \)-Fe\(_4\)N and in particular the highly metastable \( \alpha'' \)-Fe\(_{16}\)N\(_2\), which was first described by Jack \(^{33}\).
in 1953. The first report of a giant magnetic moment of the $\alpha''$-Fe$_{16}$N$_2$ film was made by Kim and Takahashi$^{34}$ in 1972 ($4\pi M_S = 26.4$ kG). The value is even higher than the greatest saturation magnetization that has been achieved in iron-based substitutional alloys in Fe$_{65}$Co$_{35}$, namely $4\pi M_S = 24.5$ kG.$^{35}$ Since then, much research has been carried out on the Fe-N films. The nitrogen-poor phases with large $M_S$, high corrosion resistance, and good mechanical properties facilitate applications of these great potential materials such as magnetic recording heads and magnetic recording media.$^{36}$ Most theoretical calculations on the crystal of $\alpha''$-Fe$_{16}$N$_2$ phase verify its giant magnetic moment. However, the high-magnetization iron nitride films are still far from real applications because of the difficulty in the phase purity and their metastable character.$^{37}$ Experimental observations also vary. Morisako$^{38}$ and Bobo$^{39}$ suggested that the nitrogen could not enhance the $M_S$, while the work done by Sun et al$^{40}$ even showed a decrease of $M_S$ of the film when nitrogen atoms were introduced into the iron film, though $\alpha''$-Fe$_{16}$N$_2$ was detected. An understanding of the nitrogen-induced magnetization enhancement is thus needed.

Size-induced magnetization deviation contributes to the physical effect, while the nitrogen catalytic-induced magnetization deviation attributes to the chemical effect. At room temperature, the $M_S$ may decrease for nanoferromagnetic materials, while nitrogen catalysis may enhance the $M_S$. A study of the joint effect of the physical size and nitrogen catalysis is therefore highly desirable.
CHAPTER 1 Introduction

1.2 Objectives

The aforementioned discrepancy in experimental and theoretical observations demands further investigation of the physical mechanism behind the size dependency. Understanding the mechanism behind the effect of nitrogen catalysis on the magnetization of iron is also important. A study of the combining effect of the physical size and nitrogen catalysis on the magnetization is highly desirable. Two correlation mechanisms provide an opportunity for this kind of further study concerning size and the effect of nitrogen catalysis on the magnetic properties of nanosolids. They are the bond-order-length-strength (BOLS) correlation mechanism for CN imperfection-induced properties variation, and the bond-band-barrier (BBB) correlation mechanism for catalysis-induced properties variation. Monte Carlo simulation, which is facilitated by great improvements in the computing speed and experimental facilities of ion beam processing laboratories, provides the simulative and experimental support for the concepts. The main objectives of this work are as follows:

(1) To study the physical mechanism behind the $M_S$ variation together with the $T_C$ suppression and coercivity ($H_C$) deviation of a ferromagnetic nanosolid.

(2) To investigate the nitrogen catalytic effect on the $M_S$ of iron thin films.

(3) To study the combining effect of the physical size and the nitrogen catalytic effect on the $M_S$ of iron films.

(4) To study the deposition of magnetic materials using the FCVA technique.
CHAPTER 1 Introduction

Theoretically, analytical solutions to the physical size and nitrogen catalytic effect on the magnetic properties based on the BOLS and BBB correlation mechanism will be derived. The discrepancy of the observations is expected to be reconciled by the model and to be verified by Monte Carlo simulation on the $M_S$ as a function of size and temperature. Experimentally, the problem of the FCVA system when it is used to deposit magnetic films will be solved. Magnetic films of various crystalline sizes will be deposited to study the size effect. Fe-N films with various nitrogen contents will be deposited to investigate the nitrogen catalytic effect on the $M_S$, and the Fe-N films with various crystalline sizes and nitrogen concentrations will be deposited to investigate the joint effect of physical size and nitrogen catalysis.

1.3 Major contributions

(i). Providing a model that incorporates the BOLS and BBB correlation mechanism into the Brillouin equation and using the “molecular field” concept, this thesis gives a basic and clear explanation for the physical size-induced $M_S$ deviations. The thesis presents the $M_S$ as a function of size and temperature, which is evidenced using Monte Carlo simulation on the spin systems of various physical sizes and geometrical shapes. It shows that, with a decrease in size, the $M_S$ of a nanosolid enhances at low temperature and decreases at temperature below $T_C$. This reconciles the discrepancy of the observations at different temperatures.

(ii). The model provides a basic understanding of the $T_C$ suppression of the ferromagnetic nanosolid by incorporating the BOLS premise into the Ising model. The same idea can also be applied to and explain well the
T$C$ suppression of the ferroelectric and superconductive nanosolid by considering a high-order of CN imperfection.

(iii). The nitrogen catalytic effect on the magnetization of iron films shows that a small amount of nitrogen improves the magnetization of iron while too much nitrogen decreases it. This reconciles the conflicting observations. For some specimens, it is even higher than the bulk value.

(iv). The joint effects of physical size and nitridation on the $M_S$ of iron films reveal that the $M_S$ of nitrogen-poor Fe-N films is higher than that of pure iron films, while the $M_S$ of nitrogen-rich Fe-N films is lower. When the grain size is larger than 8 nm, the enhancement of $M_S$ using nitriding can overcome the size-induced reduction of $M_S$. This is the first contribution in the research of nanomagnetism. It provides further understanding of nanomagnetism and offers guidelines for further study of ferromagnetic nanostructures for high-density data storage and sensor applications.

(v). The FCVA technique has many advantages and it has been applied to produce good quality and dense carbon coatings as well as metal oxide films. This thesis is the first to research the deposition of Fe-N magnetic films using the FCVA technique. The handicap of an unstable arc when depositing ferromagnetic films using FCVA has been overcome by using a unique shield for the ferromagnetic target. Various approaches to nitrogen gas introduction have been adopted, and the bias effects on surface morphology, microstructure, and magnetic properties have been studied. The work opens up avenues for further study of the magnetic films and nitriding films based on the FCVA technique.
CHAPTER 1 Introduction

1.4 Organization

The thesis starts, in chapter 1, by describing the motivation and the objectives of the research with a brief overview of the studies of physical size and nitrogen catalytic effects on the magnetic properties of ferromagnetic nanosolids. The main contributions of the thesis are also presented in this chapter.

Chapter 2 reviews the literature on the studies of physical size and nitrogen catalytic effects on the magnetic properties of ferromagnetic nanosolids of the past few decades. In accordance with the objectives of the thesis, the survey focuses on magnetization and the Curie temperature. The discrepancies in the various observations on the size effect of $M_S$, the physical and chemical mechanism behind the $T_C$ suppression of magnetic nanosolids, and the nitrogen catalytic effect on the $M_S$ of iron nanosolids are summarized.

Chapter 3 describes the three types of approaches adopted in this project, namely the theoretical, simulative, and experimental approaches. The theoretical approaches, including the BOLS, the BBB correlation mechanism, and the Ising model, are introduced. The Monte Carlo simulation method together with the simulated spins system (physical size and geometrical shapes) are also introduced in this chapter, as is the experimental FCVA technique together with the sample preparation and characterization.

In chapter 4, the physical size effects on the magnetization and $T_C$ suppression are presented in terms of the aspects of theoretical prediction, simulation, and experimentation. Several concepts are proposed for the size-induced magnetism:
(i) The magnetic moment of a surface atom is enhanced more than that of the center atoms. Electrons surrounding the lower-CN surface atoms are more localized due to the CN imperfection deepened atomic potential \(V_{\text{atom}}\) that confines electrons, which contributes to the magnetic momentum.

(ii) The exchange energy/cohesive energy (atomic CN multiplies the single-bond energy) for the lower-CN atom decreases as a result of the reduction in the number of exchange bonds; though for a single bond, the bond length is reduced and the cohesive energy per bond is enhanced.

(iii) The \(M_S\) of a solid is affected by both the magnetic moment of an individual atom and the exchange energy that determines the alignment of the spin system. At a very low temperature when the vibrational energy can be neglected, the \(M_S\) of a magnetic nanosolid increases compared with the bulk value, while at a high temperature below \(T_C\), the \(M_S\) decreases.

(iv) The coercivity \((H_C)\) of thin films increases with a decrease in grain size due to the enhancement of intergrain interaction.

(v) The decrease in the exchange energy with the size reduction contributes to the thermodynamic behavior: the \(T_C\) suppression of a ferromagnetic (ferroelectric and superconductive) nanosolid.

Chapter 5 describes the nitrogen catalytic effect on the \(M_S\) of Fe films. The chemical reaction between N and Fe transports electrons from the less...
electronegative Fe to the higher N, which enhances the magnetic moment of Fe due to the altered atomic states and hence increases the $M_S$ of the material. However, excess nitrogen decreases the $M_S$.

The joint effects of physical size and nitridation on the $M_S$ of iron films are presented in chapter 6. It is found that, in general, the $M_S$ decrease with size. With the same grain size, the $M_S$ of nitrogen-poor Fe-N films are higher than those of pure iron, while the $M_S$ of nitrogen-rich Fe-N films are lower than those of pure iron.

The thesis ends in chapter 7 with a summary of the main conclusions that are reached from having addressed the objectives outlined in chapter 1, and recommendations for further research.
CHAPTER 2 LITERATURE SURVEY

2.1 Physical size effect

2.1.1 $M_S$ suppression or elevation

Two distinguishing trends of the $M_S$ as a function of size have been reported. Some researchers observed that the $M_S$ of a ferromagnetic nanosolid decreases with the size, while other researchers, measuring the enhanced magnetic moment of a ferromagnetic nanosolid, concluded that $M_S$ enhances with the decrease in size.

2.1.1.1 Experimental observations-$M_S$ suppression

In 1976, Sumiyama et al.\textsuperscript{41} reported a remarkable reduction of $M_S$ at room temperature for Fe-Ni invar alloy thin films (<40 nm). Wedler and Schneck\textsuperscript{42} also reported a reduced $M_S$ value (1.8 kG) for very thin Ni films (<7 nm). Ohta et al.\textsuperscript{43} studied the $M_S$ for Fe$_3$O$_4$ thin films and found a rapid decrease when the film is thinner than 70 nm.

Many studies have reported a decrease in $M_S$ with size. Using the Stern-Gerlach deflections of cold iron clusters in a molecular beam, Heer et al.\textsuperscript{20} found a decrease of measured $M_S$ for small iron clusters (50–230 atoms). Bucher et al.\textsuperscript{44} used the same instrument and measured clusters in a beam as a function of cluster size ($N = 20–200$) and temperature ($T = 82–267$ K). They also found a decrease in the measured $M_S$. The same trends hold for Gd, Tb, and Dy clusters,\textsuperscript{45} Pd$_{97.1}$Fe$_{2.9}$,\textsuperscript{22} NiFe$_2$O$_4$,\textsuperscript{70,71} Ni$_3$Fe,\textsuperscript{23} Co,\textsuperscript{23} and Pd$_{96}$Fe$_4$\textsuperscript{21} nanocrystals.
CHAPTER 2 Literature Survey

Figure 2.1, for example, shows the magnetic moment of Co cluster as a function of size.\(^6^9\)

![Figure 2.1: The average magnetic moment per Co atom and the percentage of magnetic Co atoms as a function of the cluster size.\(^6^9\)](image)

2.1.1.2 Experimental observations - \(M_S\) elevation

However, opposite trends have also been observed. In 1980, Konno\(^4^6\) reported an opposite, anomalous result for Fe-Ni films. The measured \(M_S\), in a temperature range from 77 K to 570 K, showed that when the film thickness is decreased from about 75 nm to 35 nm, the \(M_S\) tends to increase gradually.

In 1985, using the laser vaporization of an iron rod inside the throat of a high-pressure pulsed nozzle, Cox et al\(^1^0\) were the first to measure the magnetic properties of isolated iron-atom clusters ranging from 2 to 17 atoms as well as the magnetic behavior of the monoxides and dioxides of (2~7) atom iron clusters. The neutral metal cluster beam passed through a Stern-Gerlach magnet and the deflected beam was detected using spatially resolved time-of-flight...
photo ionization mass spectrometry. The estimated temperature was about 22 K. They concluded that the spin per atom in the iron clusters was larger than that of bulk iron. Billas et al measured the molecular beam deflection of small iron, cobalt, and nickel clusters, and also found that the magnetic moment of the small cluster was larger than that of the bulk value. For clusters with fewer than 30 atoms, the magnetic moment is atom-like; as the size is increased up to 700 atoms, the magnetic moment approaches the bulk limit. It was then concluded that the $M_S$ of the small particle is larger than that of the bulk value. The experiments by Chen et al on Co$_n$ particles in the range of 1.8-4.4 nm showed that the magnetic moment of a 1.8 nm size particle is about 30% higher than that of the bulk. Figure 2.2 shows the measured magnetic moments of Ni$_n$ clusters. With oscillation features, the $M_S$ increases with the inverse of size.\(^\text{48}\)

![Figure 2.2 Magnetic moments of Ni$_n$ particles as a function of size, at temperatures between 73 and 198 K.\(^\text{48}\)](image)
CHAPTER 2 Literature Survey

2.1.1.3 Theories and explanations-\( M_S \) suppression

Theoretically, the \( M_S \) suppression at ambient temperature has been explained\(^{49}\) as the higher-spin temperatures of the surface spins that are weakly coupled and are more disordered at the measurement temperatures compared to the bulk spins. The \( M_S \) is then dominated by the interior bulk spins that drop in number when the solid size is decreased. Alternatively, the \( M_S \) suppression has been explained as a result of the \( T_C \) suppression of the nanosolid. In a shell structure, the surface layer is magnetically melted and contributes little to the \( M_S \) of the system.\(^{31}\) An empirical linear dependence\(^{49}\) of the specific \( M_S(K_j) \) on the specific surface area \( S(K_j) \) of the fine crystallites has been proposed in the form of:

\[
\Delta M_S(K_j)/M_S(\infty) = -A \times S(K_j)
\]  

(2.1)

where \( K_j \) is the diameter of the grain and \( A \) is a constant. Bucher et al\(^{44}\) attributed the decrease of magnetization of Co clusters to the operating temperature. The effective magnetic moment at temperature \( T \) can be expressed as:

\[
\mu_{\text{eff}} = \mu_T \left[ \coth \left( \frac{N\mu_T H}{k_B T} \right) - \frac{k_B T}{N\mu_T H} \right]
\]  

(2.2)

where \( \mu_T \) is the true magnetic moment per atom of the particle, where \( N \) is the atom number and \( H \) is the applied magnetic field.

Merikoski et al\(^{31}\) have also carried out Monte Carlo simulations on the magnetization of small ferromagnetic clusters at finite temperatures based on the Ising model. The simulation results showed that even at very low
CHAPTER 2 Literature Survey

temperature, the $M_S$ decreases with the decrease in size. The experimental observed $M_S$ reduction for isolated ferromagnetic clusters was then believed to arise from the increase of spin temperature as it was observed in the simulation.

2.1.1.4 Theories and explanations-$M_S$ elevation

For the enhancement observations at low temperature, Billas et al.$^{50}$ used a shell model and explained that the $M_S$ is enhanced as the magnetic moment of the surface layer is higher than the bulk value, which agrees with experimental observations.$^{51,52,53,54,55}$ For example, Ney et al.$^{53}$ showed that the Co surface atoms carry a moment of 2.28 $\mu_B$ per atom enhanced by 32% compared to the bulk value of 1.73 $\mu_B$ per atom. Compared to the Fe bcc bulk moment of 2.2$\mu_B$, the magnetic moment for the surface layer of Fe has been found to enhance (i) by 15% to 2.54$\mu_B$ for 1 ML Fe/5 ML W (110), and (ii) by 29% to 2.84$\mu_B$ for 2 ML Fe/5 ML W (110). The significant surface relaxation of Fe (310)(-12%)$^{56}$

Figure 2.3 Deviation from the bulk magnetic moment in (a) Fe, (b) Co, and (c) Ni as a function of nearest neighbor coordination (in various structures).$^{58}$
and Ni (210)(-12%)\textsuperscript{57} has also been found to enhance the atomic magnetic momentum by up to 27%. The magnetic moment of the surface atom was considered to be primarily determined by the local CN. Figure 2.3 shows the calculated dependence of the magnetic moment on the nearest CN using an \textit{ab initio} tight-binding theory. It is clear that as the CN decreases, the moment increases toward the atomic value.\textsuperscript{58} Table 2.1 summarizes both the experimental and the theoretical or simulating research on the size dependence of the $M_S$ of magnetic nanosolid.

The magnetic moment of ferromagnetic nanosolid as a function of size was also found to possess an oscillation with some magic numbers at which the cluster shows a particularly low magnetic moment,\textsuperscript{67,25,26,27} as shown in the Ni clusters in Figure 2.2 for example. From a theoretical point of view and with the aim to understand the oscillatory magnetic behavior of the transition metal clusters, several geometrical shell models have been proposed.\textsuperscript{25,26,27,59} In particular, in the model developed by Jensen and Bennemann,\textsuperscript{59} the individual magnetic moments of the different atoms are determined by their local atomic coordination. By assuming bulk-like structures (fcc and bcc) and different global cluster shapes (cube, octahedron, and cube octahedron), these authors found that the average magnetic moment oscillates with the cluster size, and that this magnetic “shell structure” reflects the progressive formation of concentric atomic layers. Fridel\textsuperscript{60} considers a simple rectangular d-band approximation together with the second moment approximation,\textsuperscript{61} and the assumption that the d-band splitting between the major and the minor spin caused by the exchanged interaction is invariant for the cluster to the bulk solid.
leads to the following expression\(^6^2\) for the magnetic moment as a function of the local CN in a step function:

\[
\mu_i/\mu_b = \begin{cases} 
\mu_{\text{dim}}/\mu_b, & \text{if } z_i \leq z_b \left(\frac{\mu_b}{\mu_{\text{dim}}}\right)^2 \\
\left(\frac{z_b}{z_i}\right)^{1/2}, & \text{otherwise}
\end{cases}
\] (2.3)

where \(\mu_b\), \(\mu_{\text{dim}}\), and \(\mu_i\) are the magnetic moment of an atom in the bulk, a dimmer, and the \(i\)th atomic layer, respectively. In the case of Fe, \(\mu_b = 2.22\ \mu_B\) and \(\mu_{\text{dim}} = 3.2\ \mu_B\)\(^6^3\) where \(\mu_B\) is the Bohr magneton. For \(z_b = 12\), the step function transits at \(z_i = 5.75\). Corresponding shell structures have been developed for various crystal structures\(^6^4\).

### Table 2.1 Discrepancy in the \(M_S\) as a function of size.

<table>
<thead>
<tr>
<th>Approach</th>
<th>Experimental material / theoretical approach</th>
<th>(M_S) increase ((\uparrow)) inversely with size</th>
<th>(M_S) decrease ((\downarrow)) with size</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnBi films</td>
<td>MnBi has no dependence on thickness (^6^5)</td>
<td></td>
<td>Room temperature (RT)</td>
<td></td>
</tr>
<tr>
<td>Fe-Ni films</td>
<td>(\uparrow)[46] (\downarrow)[41]</td>
<td></td>
<td>RT[41] 77 to 570 K[46]</td>
<td></td>
</tr>
<tr>
<td>Ni films</td>
<td>(\downarrow )[42]</td>
<td></td>
<td>RT</td>
<td></td>
</tr>
<tr>
<td>Fe(_3)O(_4) films</td>
<td>(\downarrow )[43] (\downarrow )[66]</td>
<td></td>
<td>RT</td>
<td></td>
</tr>
<tr>
<td>Fe, Co, Ni cluster</td>
<td>(\uparrow )[10][67][50][68][48] (\downarrow )[20][48][45][69][44]</td>
<td></td>
<td>78 to 120K 73,198K</td>
<td></td>
</tr>
<tr>
<td>NiFe(_2)O(_4) nanoparticles</td>
<td>(\downarrow )[70,71]</td>
<td>4.2 to 100K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd(<em>{97.1})Fe(</em>{2.9}) particles</td>
<td>(\downarrow )[22]</td>
<td>5 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiFe nanocrystalline</td>
<td>(\downarrow )[23]</td>
<td>&lt;150 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd(<em>{96})Fe(</em>{4}) particles</td>
<td>(\downarrow )[21]</td>
<td>4.2,100,295K</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Theory</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Self-consist-field X(\alpha)-scattered-wave molecular-orbital calculations</td>
<td>(\uparrow )[25]</td>
<td>All temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Films, all-electron self-consistent semi-relativistic full-potential linearized augmented-plane-wave local density and local-spin-density</td>
<td>(\uparrow )[27]</td>
<td>RT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tight-binding Hubbard Hamiltonian in the unrestricted Hartree-Fock approximation</td>
<td>(\uparrow )[26]</td>
<td>0 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monte Carlo simulation, Ising model</td>
<td>(\downarrow )[31]</td>
<td>&lt;(T_c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell model</td>
<td>(\uparrow )[50]</td>
<td>78 to 120K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface model</td>
<td>(\downarrow )[70,72]</td>
<td>&lt;5 K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
arrangement of atoms in different lattice structures of various solid shapes, the oscillation features could be generated using the shell model.\textsuperscript{62}

2.1.2 \( T_C \) suppression

In 1969, Morita and Taniyama\textsuperscript{73} found a drop in the \( T_C \) when the evaporated nickel films were thinner than 30 nm. \( T_C \) suppression has also been found to happen to Fe,\textsuperscript{10,74,75} Ni,\textsuperscript{14-16,76,77} Co,\textsuperscript{11,12} and Gd,\textsuperscript{17,78} thin films and \( \text{Fe}_3\text{O}_3 \) particles,\textsuperscript{79} as well as the nanocrystalline Gd\textsuperscript{80} and GdFe\textsubscript{11}Re.\textsuperscript{81,82} The tunable \( T_C \) will be an advantage for magnetic sensors or switches that can function in a given temperature range. However, the understanding of the underlying mechanism for \( T_C \)-tunability is still primitive, though models based on the criterion of SSCL limitation have been developed.\textsuperscript{28,29}

According to the scaling theory,\textsuperscript{28} the correlation length is defined as the distance from a point beyond which there is no further correlation of a physical property associated with that point. Values for a given property at distances beyond the correlation length can be considered purely random. The SSCL, \( \xi \), depends functionally on temperature as \( \xi = \xi_0 (1 - T / T_C)^\nu \), where \( \nu \) is a universal critical exponent. The SSCL limitation premise indicates that \( \xi \) is limited by the film thickness. If the \( \xi \) exceeds the film thickness \( D, \xi > K_j = D / d \), the \( T_C \) will be lower than the bulk value. \( d \) is the atomic diameter of the ferromagnetic element concerned. The SSCL mechanism gives rise to the power-law form of the \( T_C - K_j \) relation, which involves two freely adjustable parameters, \( \lambda \) and \( C \) (or \( C_0 \)), for data simulation. The \( \lambda \)-value is in the range of
1 for the mean-field approximation to 1.59 for the three-dimensional Ising model.\(^{13,28,29,83,84}\)

\[
\frac{\Delta T_c(K_j)}{T_c(\infty)} = \frac{T_c(K_j) - T_c(\infty)}{T_c(\infty)} = (C_0 K_j)^{-\lambda} \quad (2.4)
\]

In order to converge the numerical simulation with the measured data of ultra-thin films \((K_j \rightarrow 0)\), Binder, Hohenberg,\(^{84}\) and Huang et al\(^{85}\) revised Eq (2.4) by replacing the reference \(T_c(\infty)\) with the \(K_j\)-dependence \(T_c(K_j)\) for normalization. With the revised premise, numerical fit could be improved for ultra-thin films:

\[
\frac{\Delta T_c(K_j)}{T_c(K_j)} = \frac{T_c(K_j) - T_c(\infty)}{T_c(K_j)} = (C' K_j)^{-\lambda} \quad (2.5)
\]

Based on the mean field approximation, Zhang and Willis\(^{86}\) proposed an alternative to fit both the thinner and the thicker films with a step function:

\[
\frac{\Delta T_c(K_j)}{T_c(\infty)} = \frac{T_c(K_j) - T_c(\infty)}{T_c(\infty)} = \begin{cases} 
-(\frac{\xi+1}{2K_j})^2, & (K_j > \xi) \\
\frac{K_j - 1}{2\xi}, & (K_j < \xi)
\end{cases} \quad (2.6)
\]

Eq. (2.6) shows that, for \(K_j < \xi\), \(T_c\) varies linearly with \(K_j\) and if \(\lambda \neq 1\), there is a discontinuity at \(K_j = \xi\).

More recently, Nikolaev and Shipilin\(^{30}\) proposed that the ferromagnetic \(T_c\) suppression results from nothing more than the surface layer that contains atoms with only half the number of exchange bonds (CN imperfection, as termed in this presentation) per unit volume compared with the bulk. By defining a critical thickness \(\Delta R\), the \(T_c\) suppression of a ferromagnetic spherical dot can be expressed as follows:\(^{30}\)
\[
\frac{\Delta T_C(R)}{T_C(\infty)} = \frac{3\Delta R}{2R}
\] (2.7)

The quantity \(\Delta R\) was used as a parameter to characterize the number deficiency of exchange bonds for atoms at the surface region of a nanosolid. However, fitting experiment data for \(\text{Fe}_3\text{O}_4\) nanosolids of different sizes with a constant \(\Delta R\) was unsuccessful, and hence, it is suggested that the \(\Delta R\) varies with the solid size, but the \(R\) dependence of \(\Delta R\) is yet to be established.\(^{30}\)

2.1.3 \(H_C\) and \(\mu_p\)

**Coercivity:** For a freestanding nanosolid, or a single domain, the coercivity approaches zero when the size is decreased to a certain size.\(^{87,88}\) For example, \(\text{Fe}_{69}\text{Ni}_9\text{Co}_2\) powders having grain sizes of 10-15 nm show almost no hysteresis, which is suggested to be superparamagnetic,\(^{89}\) due to the long-range interaction that involves the high-order atomic \(CN\) imperfection.\(^{90}\) However, for polycrystalline magnetic materials, the superparamagnetic behavior vanishes and the coercivity appears.\(^{87,91}\) The coercivity increases with size in a \(D^6\) pattern until a critical size of 10s nm and then the \(H_C\) drops in a \(D^{-1}\) fashion when the solid grows from atomic scale to micrometer scale, and eventually approaches the bulk value.\(^{92}\) The \(D^{-1}\) fashion of \(H_C\) variation was explained by the authors as domain-wall pinning at grain boundaries. Investigation of the \(\text{Fe}_{74.5-x}\text{Cu}_x\text{Nb}_3\text{Si}_{13.5}\text{B}_9\) \((x = 0\sim1 \text{ at}\%)\) ribbons with grain sizes between 10 nm and 300 nm has shown that the \(H_C(D)\) transition from \(D^6\) to \(D^{-1}\) happens at 50 nm.\(^{92}\) Similar trends hold for Fe, Ni, and Co metal films,\(^{93}\) and the respective transition sizes are 20, 40, and 30 nm. The behavior has been explained using the random anisotropy theory.\(^{94}\)
CHAPTER 2 Literature Survey

\[ H_c \approx \frac{1}{20} \frac{K_2^4 L^6}{B M_0} \]  

(2.8)

where \( K_2 \) is the strength of local uniaxial anisotropy and \( M_0 \) is the magnitude of the local magnetization vector; \( B \) is the exchange stiffness parameter and \( L \) is the structural correlation length. Eq (2.8) applies when the magnetic scale length greatly exceeds the structural scale length. Recently, the \( H_c \) of antiferromagnetic-ferromagnetic nanostructures have also been reported to increase inversely with size.\(^95\)

**Permeability:** The initial permeability has been found to increase with decreasing gain size for several kinds of materials. For example, a study on the polycrystalline Ni\(_{0.34}\)Cu\(_{0.12}\)Zn\(_{0.56}\)Fe\(_{1.98}\)O\(_4\) with different grain sizes up to 39 \( \mu \)m found an increase of initial permeability when the grain size was reduced.\(^96\) Similarly, the initial permeability of nanocrystalline Fe\(_{86}\)Zr\(_7\)B\(_6\)Cu\(_1\) ribbons with grain sizes from 13.2 to 7.3 nm was found to increase from \( 1.2 \times 10^4 \) to \( 6.3 \times 10^4 \).\(^97\) The same tendency was found with the NiFe permalloy, as reported by See et al.\(^98\) The results were interpreted in terms of the contribution of grain boundaries and pores inside the grains to the domain wall pinning.\(^99\) However, reverse trends have also been reported.\(^100\) The changes has been modeled using the nonmagnetic grain boundary model (NMGB), which assumes a regular simple cubic distribution of cubic particles of size \( D \) separated by a gap \( \delta \),\(^101\)

\[ \mu_{p-eff} = \frac{D \mu_{p-i}}{D + \delta \mu_{p-i}} \]  

(2.9)
where $\mu_{p-i}$ is the intrinsic permeability. This model is valid only if $D >> \delta$ since only the reluctance of the particles and the air gap between them are taken into account.

### 2.2 Nitridation effect

#### 2.2.1 Iron-nitrogen system

As shown in Figure 2.4, the iron-nitrogen system consists of several interstitial solutions ($\alpha$, $\gamma$, $\varepsilon$), chemical compounds ($\gamma'$-$\text{Fe}_4\text{N}$, $\zeta$-$\text{Fe}_2\text{N}$), and metastable phases ($\alpha'$, $\alpha''$-$\text{Fe}_{16}\text{N}_2$) with various mechanical and magnetic properties. The nitrogen-poor phases are ferromagnetic compounds. In particular, the $\alpha''$-$\text{Fe}_{16}\text{N}_2$ has been reported to have a giant magnetic moment with potential applications in high-density magnetic recording media.

![Figure 2.4 Phase diagram of the Fe-N system.](image)

Figure 2.4 Phase diagram of the Fe-N system.
The α iron phase with a small amount of nitrogen solute leads to the α-Fe(N) phase. It has a maximum equilibrium solubility of interstitial nitrogen in body center cubic (BCC) iron of just 0.4 at% at 860 K. The lattice dilation in α-Fe(N) d(ln V)/dx is about 0.002, where V is the unit volume of the lattice and x is the one-dimensional lattice parameter. More nitrogen can be incorporated into the BCC lattice of thin films prepared by reactive sputtering or ion implantation. The cubic films may accommodate up to 10 at% nitrogen, with a nonuniform profile across the film. They have a microcrystalline structure with possible secondary γ'-Fe₄N and α''-Fe₁₆N₂ phases. Their 4πM₅ has been reported to be similar to, or higher than, that of α-Fe. Quenching γ-Fe(N) at 920 K will transform martensitically into the tetragonal α' nitrogen martensite (α'-Fe(N)). The greatest solubility of nitrogen in γ-Fe is 10.5%. Typically, the martensitic transformation is incomplete, and the resulting bulk material is a mixture of tetragonal nitrogen martensite and γ-Fe(N). The nitrogen in the α' phase is disordered, and it induces a lattice expansion d(ln V)/dx of 0.006. There is a continuous range of composition. Epitaxial thin films of the α' phase can be prepared directly by Molecular beam epitaxy (MBE), reactive sputtering, ion beam deposition, or nitrogen ion implantation.

Prolonged annealing (tempering) of the α' phase at about 370-420 K leads to an ordering of the nitrogen to produce α''-Fe₁₆N₂. It was first described by Jack in the early 1950s. The unit cell with a = 0.572 nm and c = 0.629 nm is doubled in all three directions. The structure was later refined by electron diffraction. Prolonged annealing or higher temperature treatment leads to decomposition of
the $\alpha''$ compound into $\alpha$-Fe and $\gamma'$-Fe$_3$N. The limited solubility of nitrogen in $\gamma$-Fe – at most, 10.5 at% – means that it is impossible to obtain a pure 16:2 phase (11.1 at%) by quenching and annealing. The giant magnetic moment of $\alpha''$-Fe$_{16}$N$_2$ was first noted by Kim and Takahashi on iron films evaporated in nitrogen ambient. Their films were a mixture of $\alpha$-Fe and the $\alpha''$ phase, and the $4\pi M_S$ of $\alpha''$-Fe$_{16}$N$_2$ was estimated to be as high as 28 kG, corresponding to an average iron moment of 3.0 $\mu_B$.

The face-centered cubic (FCC) $\gamma'$-Fe$_4$N lattice is expanded by 33% by interstitial nitrogen in the center position of FCC, giving a lattice parameter of 0.3795 nm, compared with 0.3450 nm for $\gamma$-Fe; $d(ln V)/dx = 0.017$. The nitrogen-induced expansion stabilizes a ferromagnetic state for $\gamma'$-Fe$_4$N with a $T_C$ of 767 K. At room temperature, the $4\pi M_S$ is 19 kG.

The hexagonal $\varepsilon$-Fe$_3$N has an extended homogeneity range, with a moment that decreases rapidly with increasing nitrogen content. The compound is ferromagnetic and the moment is 1.9 $\mu_B$. Orthorhombic $\zeta$-Fe$_2$N is a quasistable compound with a tiny hyperfine field of 8 kG, while metastable cubic nitrides, containing nearly 50 at% nitrogen, may have ZnS or NaCl structures. The ZnS-type nitride has been shown to be a nonmagnetic metal, while the NaCl-type nitride is an antiferromagnet. A schematic illustration of the crystal structure of $\alpha$-Fe, $\alpha''$-Fe$_{16}$N$_2$, $\gamma'$-Fe$_4$N, FeN with ZnS and NaCl structures is given in Figure 2.5.
Figure 2.5 A schematic illustration of the crystal structure of (a) \(\alpha\)-Fe; (b) \(\alpha''\)-\(\text{Fe}_{16}\)\(\text{N}_2\); (c) \(\gamma\)-\(\text{Fe}_4\)\(\text{N}_3\); (d) FeN with ZnS structure; and (e) FeN with NaCl structure.\(^{115}\) (O: Iron atom •: Nitrogen atom)
2.2.2 Synthesis of nitride films

Various deposition techniques have been used to deposit Fe-N films, such as MBE,\textsuperscript{116} multishot implantation,\textsuperscript{117} facing target sputtering,\textsuperscript{38,40} and reactive radio frequency (RF) sputtering.\textsuperscript{39} Table 2.2 summarizes the progress in the synthesis of Fe-N magnetic films or powder over recent decades. After Kim and Takahashi\textsuperscript{34} reported the giant magnetic moment of Fe\textsubscript{16}N\textsubscript{2} in 1972, much research has focused on its high magnetic momentum. Many experimental studies have been performed to confirm the giant magnetic moment.\textsuperscript{118} The results, however, vary. Komuro,\textsuperscript{144} Nakajima,\textsuperscript{117,148} Jiang,\textsuperscript{120} and Guibin\textsuperscript{125} showed that the nitrogen could enhance magnetization by 16–28\% regardless of the different deposition techniques. Wang and Zheng \textit{et al}\textsuperscript{135} recently confirmed that when little nitrogen was introduced into the iron films, magnetization increased. However, Morisako\textsuperscript{38} and Bobo\textsuperscript{39} suggested that the nitrogen could not enhance the $M_S$, while the work done by Sun\textsuperscript{40} even showed a decrease of the $M_S$ of the film when nitrogen atoms were introduced into the iron film, though $\alpha''$-Fe\textsubscript{16}N\textsubscript{2} was detected.

The theoretical studies support that nitrogen can enhance the magnetic moment of iron. Using the self-consistent linearized-augmented-plane-wave (LAPW) method within the framework of the LDA (local-density approximation), Nakajima \textit{et al}\textsuperscript{119} performed the band calculations for the Fe\textsubscript{16}N\textsubscript{2} phase. The results showed that the calculated magnetic moment was much smaller than the giant value observed experimentally. The calculated average magnetic moment was 2.35 $\mu_B$. The lattice constant dependence of the moment showed that a little
### Table 2.2 Survey of Fe-N magnetic films and powders.

<table>
<thead>
<tr>
<th>Year</th>
<th>Researchers</th>
<th>Method</th>
<th>Phases</th>
<th>4πM_s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1972</td>
<td>Kim and Takahashi</td>
<td>Evaporated in nitrogen</td>
<td>α+α″</td>
<td>26.4 kG</td>
</tr>
<tr>
<td>1984</td>
<td>Terada et al.</td>
<td>Ion beam deposition</td>
<td>Multiphases</td>
<td>24 kG</td>
</tr>
<tr>
<td>1989</td>
<td>Nakajima and Okamoto</td>
<td>Ion implantation</td>
<td>Multiphases</td>
<td>Increased</td>
</tr>
<tr>
<td>1989</td>
<td>Jiang et al.</td>
<td>Facing target sputtering</td>
<td>Multiphases</td>
<td>μ_s = 2.85μ_B</td>
</tr>
<tr>
<td>1990</td>
<td>Komura et al.</td>
<td>MBE</td>
<td>Multiphases</td>
<td>26.6 kG</td>
</tr>
<tr>
<td>1990</td>
<td>Wang et al.</td>
<td>RF-diode-sputtering</td>
<td>Multiphases</td>
<td>21 kG</td>
</tr>
<tr>
<td>1991</td>
<td>Morisako et al.</td>
<td>Facing target sputtering</td>
<td>α+γ</td>
<td>21.36 kG</td>
</tr>
<tr>
<td>1992</td>
<td>Russak et al.</td>
<td>DC magnetron sputter</td>
<td>Multiphases</td>
<td>25 kG</td>
</tr>
<tr>
<td>1994</td>
<td>Xiao and Chien</td>
<td>RF reactive sputtering</td>
<td>γ, ε and ζ</td>
<td>-</td>
</tr>
<tr>
<td>1994</td>
<td>Huang et al.</td>
<td>Treating powder in NH_3 gas</td>
<td>α+α′+α″</td>
<td>(α″)26.6 kG</td>
</tr>
<tr>
<td>1994</td>
<td>Sugita et al.</td>
<td>MBE</td>
<td>α+α′+γ</td>
<td>(α′)29 kG</td>
</tr>
<tr>
<td>1995</td>
<td>Bobo et al.</td>
<td>Reactive RF sputtering</td>
<td>Expanded α, γ, ε, ζ</td>
<td>M_γ-M_α(αFe)</td>
</tr>
<tr>
<td>1995</td>
<td>Sun et al.</td>
<td>Facing target sputtering</td>
<td>α+α′+ε+ζ</td>
<td>-</td>
</tr>
<tr>
<td>1995</td>
<td>Utsushikawa and Nizuma</td>
<td>Ion nitriding in N_2 plasma</td>
<td>α+α′+γ+ε+ζ</td>
<td>(α″) 27.77 kG</td>
</tr>
<tr>
<td>1996</td>
<td>Okamoto et al.</td>
<td>Sputter beam method</td>
<td>α′, α′+α″</td>
<td>(α′)23.3 kG (α′+α″)24.7 kG</td>
</tr>
<tr>
<td>1996</td>
<td>Sugita et al.</td>
<td>MBE</td>
<td>α″</td>
<td>μ_s = 3.5 μ_B</td>
</tr>
<tr>
<td>1996</td>
<td>Okamoto et al.</td>
<td>Sputter beam method</td>
<td>Multiphases</td>
<td>25 kG</td>
</tr>
<tr>
<td>1996</td>
<td>Niederdrenk</td>
<td>Reactive magnetron sputtering</td>
<td>e-Fe_N_1-z (0 ≤ z ≤ 0.33)</td>
<td>-</td>
</tr>
<tr>
<td>1997</td>
<td>Takahashi et al.</td>
<td>Reactive sputtering</td>
<td>α+α′+α″</td>
<td>σ_s(α″) = 240 emu/g</td>
</tr>
<tr>
<td>1997</td>
<td>Ohagai et al.</td>
<td>RF reactive sputtering</td>
<td>α+γ-Fe_N</td>
<td>24.4 kG</td>
</tr>
<tr>
<td>1997</td>
<td>Brewer et al.</td>
<td>Reactive sputtering</td>
<td>α′(54%)+α″(46%)</td>
<td>22.37 kG</td>
</tr>
<tr>
<td>1997</td>
<td>Alvarez-Fregoso</td>
<td>Electron cyclotron resonance plasma system</td>
<td>Single e-Fe_N</td>
<td>Hardness presented</td>
</tr>
<tr>
<td>1997</td>
<td>Guibin</td>
<td>Ion beam enhanced deposition (IBED)</td>
<td>α+α′+α″+γ+ε</td>
<td>-</td>
</tr>
<tr>
<td>1997</td>
<td>Ding et al.</td>
<td>Reactive ion beam sputtering</td>
<td>Highest α′/α′ phase content</td>
<td>Did not exhibit largest σ_s</td>
</tr>
<tr>
<td>1998</td>
<td>Kiriake</td>
<td>Magnetron sputtering</td>
<td>α+α′+α″</td>
<td>23.7 kG</td>
</tr>
<tr>
<td>1998</td>
<td>Ding et al.</td>
<td>Reactive ion beam sputtering</td>
<td>Multiphases</td>
<td>Enhanced but not directly related to α′+α″</td>
</tr>
<tr>
<td>1998</td>
<td>Paseka et al.</td>
<td>Ball milling in NH_3</td>
<td>α+α′+γ</td>
<td>Enhanced</td>
</tr>
<tr>
<td>2000</td>
<td>Lančok et al.</td>
<td>Nitriding powder in H_2+NH_3</td>
<td>α+α′+γ</td>
<td>-</td>
</tr>
<tr>
<td>2000</td>
<td>Yamaguschi et al.</td>
<td>Nitriding iron in ammonia-hydrogen gas at 500°C</td>
<td>Fe_N</td>
<td>σ_s = 188 emu/g</td>
</tr>
<tr>
<td>2001</td>
<td>Jirásková et al.</td>
<td>Spark erosion, plasma nitriding, and plasma immersion ion implantation</td>
<td>α(50%)+α′+α″ (20%)+γ(30%), Fe_N</td>
<td>-</td>
</tr>
<tr>
<td>2002</td>
<td>Iwatsubo et al.</td>
<td>Reactive ion beam sputtering</td>
<td>Multiphases</td>
<td>23.5 kG</td>
</tr>
<tr>
<td>2002</td>
<td>Grachev et al.</td>
<td>MBE in a flow of atomic nitrogen from an RF plasma source</td>
<td>γ-Fe_N</td>
<td>-</td>
</tr>
<tr>
<td>2003</td>
<td>Kappaganthu and Sun</td>
<td>RF sputtering</td>
<td>Multiphases</td>
<td>-</td>
</tr>
<tr>
<td>2003</td>
<td>Wang et al.</td>
<td>Magnetron sputtering</td>
<td>Fe_N, ε, FeN_1-0.96</td>
<td>Enhanced</td>
</tr>
<tr>
<td>2003</td>
<td>Nie et al.</td>
<td>RF sputtering</td>
<td>α-Fe(N), prefer (110)</td>
<td>-</td>
</tr>
</tbody>
</table>
difference in the lattice constant did not cause a substantial change in the magnetic moment. He et al\textsuperscript{137} calculated the electronic structure of Fe\textsubscript{16}N\textsubscript{2} by the linear muffin-tin orbital method in the atomic-sphere approximation (LMTO-ASA). Sakuma,\textsuperscript{138} Min,\textsuperscript{139} and Ishida et al\textsuperscript{140} also calculated the electronic and magnetic structure of Fe\textsubscript{16}N\textsubscript{2} using the same method. All of these calculations obtained an average magnetic moment of 2.4~2.5 $\mu_B$. Using the spin density functional theory, Sifkovits\textsuperscript{141} studied the chemical bonding and magnetism of iron nitride and found the following magnetic moment for various Fe and Fe nitride films (see Table 2.3).

| Table 2.3 Magnetic moment of Fe/Fe-N.\textsuperscript{141} |
|-------------|---------|---------|---------|---------|
| Fe/Fe-N     | Fe (fcc) | Fe\textsubscript{4}N | Fe\textsubscript{3}N | $\zeta$-Fe\textsubscript{2}N |
| Magnetic moment | 2.7 $\mu_B$ | 2.7 $\mu_B$ | 1.99 $\mu_B$ | 1.43 $\mu_B$ |

Many studies have also been carried out to get a high percentage of $\alpha'$ and $\alpha''$ phases in the nitride films. Bulk samples containing 30-60% $\alpha''$-Fe\textsubscript{16}N\textsubscript{2} have been produced by the quench and anneal route.\textsuperscript{109,142,143} A larger amount of $\alpha''$ phase (≥ 80%) can be stabilized in thin films grown by MBE,\textsuperscript{110,144,145,146} reactive sputtering,\textsuperscript{105,111} ion implantation,\textsuperscript{147,148} or ion beam deposition.\textsuperscript{149,150}

Borsa et al\textsuperscript{151} have developed an all-nitride magnetic tunnel junction. However, only the primary results of the growth and properties of $\gamma$-Fe\textsubscript{4}N, $\alpha''$-Fe\textsubscript{16}N\textsubscript{2}, and Cu\textsubscript{3}N were reported. Epitaxial $\gamma$-Fe\textsubscript{4}N films were grown by MBE of iron in the presence of atomic nitrogen from an RF atomic source. Layers of Cu\textsubscript{3}N were grown in a similar fashion. The $\alpha''$-Fe\textsubscript{16}N\textsubscript{2} phase was synthesized by nitriding
epitaxial iron layers. At that time, no pure Cu$_3$N or α”-Fe$_{16}$N$_2$ phase could be obtained.

From the above survey of the literature, it can be seen that further investigation of the size-induced magnetic properties of ferromagnetic nanosolids that could reconcile the discrepancy and provide a better basic understanding is highly desirable. The nitridation effect on the iron films also needs further investigation. In particular, the joint effect of physical size and nitridation should be examined. As the objectives listed in section 1.2, this thesis investigates these aspects.
CHAPTER 3  APPROACHES

Three approaches have been used in this study: theory/model, simulation, and experiment. The theories/models approach is based on the BOLS correlation mechanism, the BBB correlation mechanism, and the Ising model. The Monte Carlo simulation, which incorporates the BOLS correlation mechanism into the Ising model, is applied to study the size and temperature influence of the magnetic properties of a nanosolid. Experimentally, the FCVA technique is applied to deposited magnetic thin films of various grain sizes and Fe-N films with various nitrogen contents to investigate the physical size effect and the nitrogen catalytic effect on the magnetization, respectively.

3.1 Theory

3.1.1 BOLS correlation

The BOLS correlation mechanism\textsuperscript{152,153} attributes the origin of the physical properties of a nanosolid to the CN imperfection of atoms at the surface or at the site surrounding defects. It is known that the CN imperfection at a surface site causes the remaining bonds of the atom to contract spontaneously corresponding with an enhancement of bond energy.\textsuperscript{154,155} The bond energy rise contributes not only to the cohesive energy ($E_{\text{coh}}$) but also to the energy density in the relaxed surface region. The $E_{\text{coh}}$ relates to thermodynamic properties such as self-assembly growth, diffusion, chemical reactivity,\textsuperscript{156} melting,\textsuperscript{157} and phase transition.\textsuperscript{158,159} The energy density rise per unit volume in the relaxed region will contribute to the Hamiltonian, which determines such aspects as the entire band structure (band gap and core-level shift),\textsuperscript{160,161,162} mechanical strength,\textsuperscript{156}
phonon frequency, and the dielectrics of a nanosolid of which the surface curvature and the portion of surface atoms vary with particle size.\textsuperscript{163,160,161}

The CN imperfection-induced bond relaxation can be defined as \( d_i = c_i d \) by introducing a coefficient \( c_i < 1 \) for bond contraction and \( c_i > 1 \) for bond expansion. The bond contraction and the response of bond energy can be expressed as:

\[
\begin{align*}
\frac{\Delta d_i}{d} &= c_i - 1 < 0; \\
\frac{\Delta \varepsilon_i}{\varepsilon} &= \varepsilon_i - 1 = c_i^{-m} - 1 > 0 \\
\varepsilon_i &= \frac{2}{1 + \exp[(12 - z_i) / 8z_i]}
\end{align*}
\]  \hspace{1cm} (3.1)

where \( c_i \) is the bond contraction ratio that is a function of CN, \( z_i \).\textsuperscript{164} Subscript \( i \) denotes the \( i \)th atomic layer, which may be counted up to three from the outermost atomic layer to the center of the solid as no CN reduction is expected for \( i > 3 \). The \( m \) describes the bond-length dependence of the binding-energy change, \( \varepsilon = c_i^{-m} \varepsilon \), at equilibrium atomic separation, as illustrated in Figure 3.1. The \( c_i^{-m} \) is independent of the types of interatomic potential. Previous research has revealed that for elemental solids, \( m = 1 \); for compounds and alloys, \( m = 4 \).\textsuperscript{165,166} The \( d \) and \( \varepsilon \) are the corresponding bulk values.

The CN dependence of the reduced bond length is shown in Figure 3.2. The bond contraction is about 12\%, 6\%, and 3\% when the CN of the atom is reduced from 12 to 4, 6, and 8, respectively. CN imperfection and bond contraction happen at any site where a structure defect exists such as an amorphous state. However, in a bulk crystal, this effect is negligible because of
the small \( S/V \) ratio. With the size reduction, the \( S/V \) ratio increases. This causes the surface atoms to play an increasingly dominant role in the nanomaterial. The \( S/V \) ratio of the \( i \)th surface layer can be expressed as:

\[
\gamma_i = \frac{N_i}{N_j} = \frac{V_i}{V} = \frac{R_{i-out}^n - R_{i-in}^n}{R_{i-out}^n} \tag{3.2}
\]

where \( n \) is the dimensionality of a nanosolid and \( R = K_Jd \) is the radius of a rod \((n = 2)\) or a spherical dot \((n = 3)\), or a thin plate \((n = 1)\). The \( R_{i-out} \) or \( R_{i-in} \) corresponds to the outer or inner radius of the \( i \)th atomic layer with respect to the center of the solid. The \( N_i \) and \( V_i \) are the atom number and the volume of the \( i \)th surface layer, respectively. \( N_j \) and \( V \) are the whole atom number and the volume of the nanosolid, respectively.

Figure 3.1 Schematic illustration of the effect of atomic CN imperfection on the bond length and atomic trapping potential well depth of the lower-coordinated atoms near the edge of a surface. The deepened atomic potential \((V_{atom})\) confines electrons that contribute to the magnetic momentum of the lower-CN atoms. \( \delta_{surf} \) is the perturbation to the crystal potential \((V_{crystal})\) due to CN imperfection.\(^{153}\)
CHAPTER 3 Approaches

Figure 3.2 CN dependence of bond contraction derived from Goldschmidt’s premise, and findings of Feibelman (open square)\textsuperscript{164} in which CN = 12 is the standard.\textsuperscript{165}

Generally, the mean relative change of a traditional quantity $Q$ of a nanosolid containing $N_j$ atoms, with dimension $K_j$, can be expressed as $Q(K_j)$, and as $Q(\infty)$ for the same solid without surface relaxation. The $Q(K_j)$ relates to $Q(\infty) = N_jq$ using a shell structure as follows:

\[ Q(K_j) = (N_j - N_s)q + N_s q_s = N_jq + N_s(q_s - q) \]  \hspace{1cm} (3.3)

The $q$ and $q_s$ correspond to the density of $Q$ inside the bulk and in the surface region, respectively. $N_s = \sum N_i$ is the number of atoms in the surface atomic shells. Eq. (3.3) leads to the immediate general expression of size-induced change of physical properties $Q$: 

\[ Q = (N_j - N_s)q + N_s q_s \]
The weighting factor, $\gamma_i$, is the S/V ratio (see Eq. (3.2)) that changes with the dimension ($K_j$) and dimensionality ($n$) of the solid.

### 3.1.2 BBB correlation

The details of the BBB correlation mechanism are described in reference [152]. Briefly, the BBB correlation mechanism initiated and verified that an oxygen or nitrogen atom hybridized its $sp$ orbitals upon reacting with a solid surface. In the process of oxidation/nitridation, nonbonding lone pairs, antibonding dipoles, and hydrogen-like bonds are involved, which add corresponding density-of-states (DOS) features to the valence band of the host. The modified valence state should contribute to the magnetization of a ferromagnetic solid.

### 3.1.3 Ising model – exchange interaction

For a magnetic system, the Ising model\(^{168}\) supposes that electron spins take up and down orientations. The model applies a simple classical assumption to an atomic or electronic magnetic moment, which can take two values:

$$s_j = \begin{cases} +1, & \text{spin up} \\ -1, & \text{spin down} \end{cases} \quad (3.5)$$
The force between two magnets falls inversely with the atomic distance. A reasonable approximation is to assume that any spin interacts only with its nearest neighbors. The interaction energy can be approximated by:

\[ E = -\sum_{i<j} J_{\text{exc}} s_i s_j - H \sum_i s_i \]  

(3.6)

If the interaction strength \( J_{\text{exc}} > 0 \), the system is ferromagnetic. The energy is minimized if the spins point in the same direction \( s_i s_j = +1 \). If \( J_{\text{exc}} < 0 \), the system is antiferromagnetic. \( H \) represents an external magnetic field which couples to the magnetization:

\[ M = \sum_i s_i \]  

(3.7)

### 3.2 Monte Carlo simulation

#### 3.2.1 Introduction

Monte Carlo simulation is a stochastic technique used to solve mathematical problems. The word "stochastic" means that it uses random numbers and probability statistics to obtain an answer. Monte Carlo methods randomly select values to create scenarios of a problem. These values are taken from within a fixed range and selected to fit a probability distribution (e.g. bell curve, linear distribution, etc.). In Monte Carlo simulation, the random selection process is repeated many times to create multiple scenarios. Each time a value is randomly selected, it forms one possible scenario and solution to the problem. These scenarios give a range of possible solutions, some of which are more probable and some less. When repeated for many scenarios (10,000 or more), the average solution will give an approximate answer to the problem. The
accuracy of this answer can be improved by simulating more scenarios. In fact, the accuracy of a Monte Carlo simulation is proportional to the square root of the number of scenarios used.

3.2.2 Methodology

Monte Carlo simulation of the magnetic system is based on the Ising spin system. Many interesting magnetic properties are related to the dynamics of the spin system. At low temperatures, the magnetic moment (or total electronic spin) of the system may spontaneously change direction in a quantum process. At higher temperatures, the spin direction will fluctuate due to thermal agitation. Meanwhile, the magnitude of the magnetic moment will decrease, and eventually vanish at the Curie temperature. However, spin dynamics in magnetic systems is still a topic of great theoretical interest and remains controversial.

• Configuration of sample

One sample or configuration of the magnet is a particular assignment of spin values, say:

\[ s_i = \pm 1 \]  

in which each spin is set either “up” or “down.” According to statistical mechanics, the average value of an observable is obtained by weighting each configuration with the Boltzmann factor, $k_B$. For example, the average magnetization at some fixed temperature $T$ is given by:
CHAPTER 3 Approaches

\[
\langle M \rangle = \frac{\sum_{\text{configs}} Me^{-E/k_B T}}{\sum_{\text{configs}} e^{-E/k_B T}} \quad (3.9)
\]

- **Configuration space**

The total number of configurations of a system is enormous even for a small number of spins. For example, for a system with 20 shells, the layer number \(K_j\) \((R / d)\) is about 5.0. The total spin number, \(N_j\), is 555, and the

\[
\text{No. of configs} = 2^{N_j} = 2^{555} = 1.18 \times 10^{167} \quad (3.10)
\]

If we enumerate the configurations at one billion per second on a very fast computer, it would take \(1.18 \times 10^{158}\) seconds, or \(3.74 \times 10^{150}\) years to compute the average magnetization exactly.

- **Probability distribution**

The basic idea of a Monte Carlo calculation is to generate a reasonable number of configurations at random. The Boltzmann factor is an exponential function of energy, which can vary enormously. The random configurations are therefore generated with probability determined by the following factor:

\[
p(s_1, s_2, ..., s_{N_j}) = \frac{e^{-E(s_1, s_2, ..., s_{N_j})/k_BT}}{\sum_{\text{configs}} e^{-E/k_B T}} \quad (3.11)
\]

- **Monte Carlo average**

The problem now is to generate \(N_j\) statistically independent configurations that are distributed according to the Boltzmann factor:
3.2.3 The algorithm of Metropolis

For simplicity, the method to generate configurations distributed according to the Boltzmann factor that was proposed by Metropolis et al\(^{174}\) was used in the simulation. According to this method, the algorithm generates the next configuration in the sequences as follows. Given a configuration, choose a spin \(s_i\), let \(s_{i,\text{trial}} = -s_i\), and compute the change in energy of the system:

\[
\Delta E = E(s_1, s_2, ..., s_{i,\text{trial}}, ..., s_{N_j}) - E(s_1, s_2, ..., s_i, ..., s_{N_j})
\]  

(3.15)

If

\[
e^{-\Delta E/k_B T} > r
\]  

(3.16)

then flip this spin, let \(s_i \leftarrow s_{i,\text{trial}}\), where \(r\) is a uniform random deviation. Repeating the above iteration for all \(N_S\) spins in the configuration, from a certain initial configuration, after a suitable number of Monte Carlo steps, the system can reach a thermally stable state and the statistical averages can be obtained. In this study, 5000 Monte Carlo steps are carried and it is enough to get the stable state.
3.2.4 Spin system

Six kinds of nanosolid systems have been employed to investigate the size and shape effect on the magnetization at various temperatures: fcc spherical particles, fcc rod, fcc plate, icosahedron particles, Marks decahedron particles, and fcc truncated icosahedron particles.

The fcc spherical particles are formed such that layers of successive neighbors are added to an atom in the center. The example in Figure 3.3 shows two fcc spherical particles, $N_{135}$ and $N_{141}$, with shell numbers $S = 8$ and $9$ and diameters $K_j = 3.1$ and $3.3$ in the unit of $d$, respectively. The oscillation of the number of atoms in the first outer shell reflects the different degrees of structure openness. Here, only those clusters with complete shells were considered, as in Merikoski et al. Table 3.1 shows the first 24 spherical particles.

![Example structure of fcc dot.](image)

(a) $N_{135}$: $S = 8$, $K_j = 3.1$

(b) $N_{141}$: $S = 9$, $K_j = 3.3$

Figure 3.3 Example structure of fcc dot. The red atoms belong to the first outer shell. The atoms in the first outer layer of $N_{141}$ are much fewer in number than those of particle $N_{135}$, indicating the oscillations of the surface state when a particle is growing up.
The rod and the plate spin systems are also formed based on the fcc lattice. The axis of the rod system is arbitrarily chosen \(<100>\) direction and the length is maintained at \(K_j = 28.3\). The radius ranges from \(S = 1\) to \(11\) \((K_j = 0.5\text{~}3.66)\), as, for example, in Figure 3.4 (a), which shows an fcc rod with \(S = 3, K_j = 1.9\). The orientation of the plate is also in \(<100>\) direction and the width and length are maintained at \(K_j = 28.3\). The thickness ranges from \(S = 1\) to \(14\) \((K_j = 0.5\text{~}5.1)\), as shown in Figure 3.4 (b).

There are three main types of ordered structures: icosahedra, decahedra, and close-packed octahedra, which are favored by nanosolids from an energetic point of view (see Figure 3.5 (a)\text{~}(c) for \(N_{147}, N_{101}, \text{and } N_{201}\)). Icosahedra and decahedra are

**Table 3.1** Magnetic nanoparticle systems for Monte Carlo simulation (R is the radius of the particle, \(N_i\) is the atomic number of \(i\)th shell, \(N_j\) is the atomic number of the whole particle, and \(z_i\) is the CN of the atoms in the \(i\)th shell).

<table>
<thead>
<tr>
<th>Shell number</th>
<th>(K_j(R/d))</th>
<th>(N_j)</th>
<th>(N_j = \sum N_i)</th>
<th>(z_i(N_j=55))</th>
<th>(z_i(N_j=135))</th>
<th>(z_i(N_j=225))</th>
<th>(z_i(N_j=683))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
<td>12</td>
<td>12</td>
<td>12</td>
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<td>2</td>
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<td>12</td>
<td>13</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>1.914214</td>
<td>6</td>
<td>19</td>
<td>8</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>2.232058</td>
<td>24</td>
<td>43</td>
<td>7</td>
<td>12</td>
<td>12</td>
<td>12</td>
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<tr>
<td>5</td>
<td>2.499981</td>
<td>12</td>
<td>55</td>
<td>5</td>
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<td>12</td>
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<td>3.145781</td>
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<td>683</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
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</tbody>
</table>
noncrystalline structures that cannot be found in bulk crystal because of their fivefold symmetry. Icosahedra are quasispherical structures, where atoms are arranged in concentric shells. They present six fivefold symmetry axes and have only (111) facets. Decahedra, which have a single fivefold axis, are less spherical than icosahedra. Their standard form contains a large amount of atoms set in (100) facets whose energy is higher than those set in (111) facets, and thus is not favored. The much more optimized form is Marks-truncated decahedra, where reentrant (111) facets are introduced via a modified-Wulff construction to optimize the nanosolids’ energetic stability.

Figure 3.5 The illustration of (a) Icosahedron $N_{147}$, (b) Marks decahedron $N_{101}$, and (c) fcc truncated octahedron $N_{201}$.\textsuperscript{175}
Close-packed nanosolids, which own the crystalline structure, have even larger surface energy because of the wide-open (100) facets that are necessary to build up a quasispherical structure. In addition to the fcc spherical dot, three kinds of particles were used for MC simulations, as listed in Table 3.2. Appendix I is the Monte Carlo calculation code for simulating the size and temperature effect on the magnetic behavior of ferromagnetic nanosolids.

Table 3.2 Icosahedron, Marks decahedron, and fcc truncated octahedron particles used in MC simulation.

<table>
<thead>
<tr>
<th>Icosahedron</th>
<th>Marks decahedron</th>
<th>Fcc truncated octahedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_{13} )</td>
<td>( N_{75} )</td>
<td>( N_{19} )</td>
</tr>
<tr>
<td>( N_{55} )</td>
<td>( N_{101} )</td>
<td>( N_{38} )</td>
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<td>( N_{318} ) #</td>
<td>( N_{79} )</td>
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<td>( N_{389} ) #</td>
<td>( N_{201} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( N_{225} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( N_{260} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( N_{314} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( N_{405} )</td>
</tr>
</tbody>
</table>

# Decahedron; * Fcc octahedron

3.3 Experimental details

3.3.1 Filtered Cathodic Vacuum Arc (FCVA) system

Figure 3.6 shows the FCVA system used for the film deposition. Figure 3.7 provides a schematic illustration of the off-plane double bend (OPDB) FCVA. The system mainly consists of three parts: a cathodic arc source, a plasma-filtering duct, and a deposition chamber. A rotary-cryogenic pump system is connected to the chamber for pumping down to the desired pressure during the deposition. The cathodic vacuum arc source has five main parts: the anode wall,
CHAPTER 3 Approaches

the power supply, the arc trigger, the target, and the target cooling system.

Before deposition, the

Figure 3.6 The FCVA system with two six-inch diameter OPDB filters (R&D)

Figure 3.7 Schematic illustration of the FCVA system
chamber is prepumped down to a pressure less than $10^{-5}$ torr. The power supply is an electrical welding machine with a maximum current of 250 A. The anode is grounded (deposition chamber) and the cathode is connected to the target. A radial electric field is formed via the toroidal duct, coupled with a curvilinear axial magnetic field on the curved toroidal duct that forms a crossed electric-magnetic field filtering assembly. The plasma, which is steered by the field, passes through the duct to the substrate and results in the deposition of films free from any unwanted macroparticles and neutral atoms. The ions are highly energetic, with kinetic energies typically of 50-150 eV, which is considerably higher than those of the evaporated or sputtered atoms, even though the discharge voltage is only around 20 V. The high ionization facilitates controlling the energy of the depositing ions by biasing the substrate which has a strong influence on the microstructure of the coating, while the high energy results in self-cleaning of the substrates of contaminants by ion sputtering. The high flux results in a high deposition rate which is economically favorable. The FCVA technique combined with an OPDB filter has the following advantages over other deposition techniques:

a) The working pressure is very low (below $1 \times 10^{-5}$), which results in a clean deposition.

b) The OPDB filter enables high-quality, macroparticle-free film deposition.

c) The ion energy is high and adjustable.

d) The deposition rate is high.
3.3.2 Shield for magnetic target

Generally, for nonferromagnetic metal and carbon targets, the arc is easy to be maintained in a stable state, while for the ferromagnetic metal target, the arc is unstable because the high permeability of the target changes the distribution of the magnetic field around the cathode. When the ferromagnetic target is used, the magnetic flux concentration at the edge of the target is high, resulting in the arc point’s running around the edge of the target during sputtering. This extinguishes the arc after a short time. To solve this problem, a shield is designed and applied around the target, as shown in Figure 3.8. The shield for the cathode consists of

![Diagram of modified cathode](image)

Figure 3.8 Schematic illustration of the modified cathode for the magnetic target. The cathode consists of the target and its supporter with a water-cooling system. The shield consists of three main parts: the aluminum cylinder, the pure iron O-ring, and the BN O-ring.
three main parts: the aluminum cylinder, the pure iron ring, and the BN O-ring. The metal cylinder covers the cathode target and the copper supporter near the cooling water systems. The outer bend wall is connected to the anode. The shield is in a floating potential that separates the electrical field between the cathode and the anode into two parts. The configuration prevents the plasma from being formed in this area. The ring of pure iron provides a larger virtual target surface, which results in a stable arc spot. The BN O-ring is set on top of the aluminum cylinder. The inner diameter of the BN O-ring is 60 mm, which can shield the target well and stop the arc from being extinguished. Furthermore, the BN O-ring possesses very low surface energy that facilitates the erasure of the residua after deposition.

The target surface that does not have the shield is consumed at the edge, while the target surface with the shield is consumed from the center of the top surface, indicating the effectiveness of the shield, as shown in Figure 3.9.

![Figure 3.9 Magnetic targets (a) with and (b) without using the designed shield.](image)
3.3.3 Sample preparation

- Nickel thin films

Ni thin films with different thickness and grain sizes were deposited on Si(001) substrates using the FCVA technique by controlling the substrate temperature from 100 to 400°C. The magnetic properties were studied to verify the size effect on the magnetization at room temperature. Ni was chosen instead of Fe because Ni has relatively high oxidation resistance compared with Fe. A pure nickel cylinder (99.9%) with dimensions of $\phi 60 \times 20$ mm was mounted on the water-cooled copper support as the cathode target. The arc current was maintained at 120 A. The basic vacuum was around $1 \times 10^{-5}$ torr. The films thickness was below 124 nm.

- Fe-N thin films with various nitrogen concentrations

Fe-N films with various nitrogen concentrations were deposited to investigate the nitridation effect on the $M_S$ of iron films. Three approaches were applied to obtain the nitrogen concentrations: (i) The nitrogen gas was input directly into the chamber. Experimental results showed that only $\alpha$-Fe(N) phase was formed in the iron films with very low nitrogen concentration. (ii) Nitrogen was introduced into the plasma area on top of the iron target. Nitrogen-poor phases were formed in the films using this approach. (iii) A linear ion beam source (D.C. $2.5 \times 20$ cm$^2$) was introduced into the chamber to produce dense nitrogen ions. The nitrogen ions, together with the iron plasma produced by the cathode source, reached the substrate and formed the ion-assisted FCVA deposition. Nitrogen-rich phases such as FeN were obtained in the films. The details of the deposition conditions are listed in Table 3.3. The three aforementioned
 CHAPTER 3 Approaches

deposition methods are illustrated in Figure 3.10. Using these approaches, the nitrogen partial pressure \( (P_N) \) and the argon to nitrogen ratio \( (P_N : P_{Ar}) \) can be controlled, and hence Fe-N films with different nitrogen concentrations can be produced. During the deposition, the substrate temperature was maintained at around 150°C. The arc current was maintained at 120 A.

- \( \alpha \)-Fe(N) films under various bias voltages

For FCVA deposition, the plasma that reaches the substrate is highly ionized and free of macroparticles and neutral atoms, which facilitate a deposition with controllable ion energy. The intrinsic energy of ions emitted from a cathode source is considerably higher than that of evaporated or sputtered atoms. The energy of ions is a very important parameter during the deposition, which affects the films in terms of deposition rate, surface morphology, microstructure, magnetic properties, and so forth. To systematically study the bias effect on the

<table>
<thead>
<tr>
<th>Approach for N introduction</th>
<th>Sample No.</th>
<th>Working pressure (torr)</th>
<th>( P_N : P_{Ar} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I: Deposition chamber</td>
<td>I-1</td>
<td>2.0 \times 10^{-4}</td>
<td>100:0</td>
</tr>
<tr>
<td>II: Plasma area in cathode source</td>
<td>II-1</td>
<td>2.0 \times 10^{-4}</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>II-2</td>
<td>1.5 \times 10^{-4}</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>II-3</td>
<td>1.0 \times 10^{-4}</td>
<td>100:0</td>
</tr>
<tr>
<td></td>
<td>II-4</td>
<td>0.7 \times 10^{-4}</td>
<td>100:0</td>
</tr>
<tr>
<td>III: Ion beam source</td>
<td>III-1</td>
<td>2.2 \times 10^{-4}</td>
<td>100:7</td>
</tr>
<tr>
<td></td>
<td>III-2</td>
<td>2.0 \times 10^{-4}</td>
<td>80:7</td>
</tr>
<tr>
<td></td>
<td>III-3</td>
<td>1.8 \times 10^{-4}</td>
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<td>III-7</td>
<td>1.0 \times 10^{-4}</td>
<td>10:7</td>
</tr>
</tbody>
</table>
properties of iron nitride films, \(\alpha\)-Fe(N) films were deposited at bias voltages of 0, –50, –100, –200, and –400 V by maintaining the working pressure at \(5 \times 10^{-5}\) torr and \(P_{N_2} : P_{Ar} = 100:0\).

Figure 3.10 The three approaches introducing nitrogen gas: (I) nitrogen is introduced directly into the chamber; (II) nitrogen is introduced into the plasma region near the target; and (III) nitrogen is introduced into the linear ion beam source.
Fe-N films of various grain sizes

The combining effects of physical size and nitrogen catalysis were examined by introducing different nitrogen concentrations and controlling different grain sizes on the Fe-N films. The films with low nitrogen content were deposited using approach II at a nitrogen flow rate of 50 sccm. The films with high nitrogen content were deposited using approach III with N₂:Ar = 50:7 and a working pressure of $1.8 \times 10^{-4}$ torr.

The substrate temperature varied from 100 to 400°C.

Table 3.4 summarizes the deposition conditions of the Fe-N samples together with the pure iron films. The films thickness is ~80 nm.

<table>
<thead>
<tr>
<th>Series</th>
<th>Nitrogen introducing approaches</th>
<th>Working pressure</th>
<th>Substrate temperature (°C)</th>
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<tbody>
<tr>
<td>Pure iron (Fe)</td>
<td>-</td>
<td>$1.0 \times 10^{-4}$ torr</td>
<td>110 230 350</td>
</tr>
<tr>
<td>Nitrogen poor: Fe-(N-Poor)</td>
<td>Approach II</td>
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<td>110 170 230 290 350</td>
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<tr>
<td>Nitrogen rich: Fe-(N-Rich)</td>
<td>Approach III</td>
<td>$1.8 \times 10^{-4}$ torr</td>
<td>100 200 300 400</td>
</tr>
</tbody>
</table>

### 3.3.4 Characterization methods

- **Thickness**

The Surface Profile Measuring System (TENCOR P-10) was used to measure the thickness of the films. Before deposition, marks were made on the surface of the substrate by a sign pen. After deposition, film deposited on the marked part was removed, which formed a steep step for thickness measurement. The
area of the sample for magnetic measurement was also obtained from the surface profile measuring system. The value of the rectangular coordinate for each point of the polygon was measured and the area was then calculated.

- **Surface morphology**

  Atomic Force Microscopy (AFM) (Dimension 3000 Scanning Probe Microscope, Digital Instruments) was used to measure the surface morphology of the films. The Root Mean Square (RMS) roughness was obtained from the digital image-processing package of the AFM system.

- **Microstructure and grain size**

  The microstructures of the films were characterized using the Siemens D5005 X-Ray diffraction (XRD) with a glancing incident mode by using CuKα (λ = 0.154 nm) radiation (40 kV, 40 mA). The incident angle was fixed at 1°, the 2θ scanning step size was set at 0.05°, and the counting time at each step was 2 s. The grain size was calculated from the full width at half maximum (FWHM) of the peak (radians) using Scherrer’s equation: 
  
  \[ t = \frac{C \lambda}{B \cos \theta} \]

  where \( \lambda \) is the x-ray wavelength (nm), \( B \) is the FWHM of the peak (radians) corrected for instrumental broadening, \( \theta \) is the Bragg angle, \( C \) is a factor (typically 1.0) that depends on the crystallite shape, and \( t \) is the crystallite size (nm).

- **Binding energy and nitrogen concentration**

  The binding energy and the nitrogen concentration were characterized by X-ray photoelectron spectroscopy (XPS). The XPS analysis was performed using a Kratos-Axis spectrometer with Dual-Anode Al Kα (1486.6 eV) X-ray radiation.
CHAPTER 3 Approaches

(150W, 15 kV, and 10 mA) and a hemispherical electron energy analyzer. The base pressure of the chamber was $2 \times 10^{-9}$ torr. The survey spectra in the range of 0-1100 eV were recorded in 1 eV step for each sample, followed by high-resolution spectra over different element peaks in 0.1 eV step, from which the detailed composition was calculated. Curve fitting was performed after a Shirley background subtraction by nonlinear least square fitting using a mixed Gauss/Lorentz function. To remove the surface contamination layer, Ar ion bombardment was carried out for 480 seconds using a differential pumping ion gun (Kratos MacroBeam) with an accelerating voltage of 4 keV and a gas pressure of $1 \times 10^{-7}$ torr. The bombardment was performed at an angle of incidence of $45^\circ$ with respect to the surface normal.

- **Magnetic properties**

The Vibrating Sample Magnetometer (VSM) was used to measure the magnetic properties of the films. The output of the VSM is a hysteresis loop. The VSM measures the total magnetic moment, $m_{emu}$, of a sample in emu (electromagnetic unit), and this result may be related to the sample magnetization using the definition of the emu: $1$ emu = $1$ Gauss-cm$^3$. The magnetization, $M$, is determined by dividing the sample moment, $m_{emu}$, by the sample volume, $V$, as shown in: $M$ (Gauss) = $m_{emu}$ (emu = Gauss-cm$^3$) / $V$ (cm$^3$).
CHAPTER 4   RESULTS AND DISCUSSION I:

PHYSICAL SIZE EFFECT

In this chapter, the physical size effects are introduced in four sections. In the first section, theory analysis and prediction for the size-induced $M_S$ shift and $T_C$ suppression are presented by incorporating the BOLS correlation prediction into the Brillouin equation and Ising model. In the second section, simulation results obtained from the MC calculation on the spin systems with various physical sizes and geometrical shapes are shown. Both the $M_S$ shift at various temperatures and the $T_C$ shift are exhibited. The third section describes how the Ni films with various grain sizes that are deposited using the FCVA technique. The size effects on the $M_S$ and $H_C$ at ambient are introduced. In the last section, the model of $T_C$ suppression for ferromagnetic nanosolids is extended to ferroelectrical and superconductive nanosolids by considering the high order of CN imperfection in the BOLS correlation mechanism.

4.1   BOLS prediction

4.1.1   $M_S$ variation

- Enhancement of surface magnetic moment

The spin distribution is based on the Hund’s rules, which are a set of guidelines for finding the lowest energy state of an atom. The rules are empirical but have theoretical justification in quantum mechanics.

Hund’s first rule asserts that the state with the highest spin has the lowest energy; when several states have the same spin, the state with the highest orbital
angular momentum has the lowest energy. Hund’s second rule is that, in the
lowest energy state of a shell that is less than half full, \( J \) has its maximum
value.\(^{179}\) Hund’s first rule requires that the spin is maximized, so that for an Fe
atom \((3d^64s^2)\), there are five electrons on the 3d spin-up levels, two occupying
the 4s levels, and the rest on the 3d spin-down levels. The spin quantum number
\( S = 4 \times \frac{1}{2} = 2 \). The angular momentum quantum number \( L = 2 + 2 + 1 + 0 + (-1)
+ (-2) = 2 \). Hence, the total angular momentum \( J = S + L = 4 \). The Lande’s g-
factor is calculated by the following expression:\(^{179}\)

\[
g_J = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} \quad (4.1)
\]

For an Fe atom, it is easy to get \( g_J = 3/2 \). The magnetic moment can then be
calculated as follows:\(^{179}\)

\[
\mu_J = g_J \sqrt{J(J + 1)} \mu_B = 6.7 \mu_B \quad (4.2)
\]

The maximum magnetic moment in the direction \((z)\) axis of the applied
magnetic field is: \( \mu_{J_z} = g_J \mu_B = 6 \mu_B \). However, in the bulk, the situation changes
because the L-orbital is frozen, \( L = 0 \).\(^{179}\) When the metal atoms come closer
together, the discrete localized atomic orbitals become delocalized, resulting in
cohesion of the atoms, and the discrete atomic levels disperse in energy, giving
rise to energy bands. In the bulk, each atom contributes (essentially) one
electron to the 4s band (in contrast to the atom). The 3d electrons remain
reasonably localized and retain much of their atomic character. Following an
approximation carried out by Billas \textit{et al},\(^{50}\) we assume that the 3d orbitals are
not delocalized at all and hence the 3d metals are atom-like. In that case, the 3d
spin-up band is fully occupied (with five electrons per atom) and has two spin-

\[\text{CHAPTER 4 Physical Size Effect}\]
CHAPTER 4 Physical Size Effect

down electrons per atom. The spin imbalance is simply the difference in the number of spin-up and spin-down 3d electrons per atom. Consequently, the magnetic moment per atom for Fe is 3 \( \mu_B \). This has been measured by Billas et al.\(^{50} \)

Different from the bulk picture, clusters have a large portion of atoms on the surface where the electronic structure is different. This is due to the reduced number of nearest neighbors, which causes the 3d electron to be more localized.\(^{180} \) The BOLS correlation mechanism, as described in section 3.1.1, indicates that the CN imperfection of an atom at the surface or at the site surrounding the defect causes the remaining bonds of the lower-coordinated atom to contract spontaneously, which is associated with a magnitude increase of the bond energy or potential well deepening. Consequently, the binding energy density in the relaxed region is higher than that in the bulk region, while the cohesive energy \( (E_{coh,i} = z_i E_i) \) of the lower-coordinated \( (z_i) \) atom is weakened, though the individual bond energy is increased. As illustrated in Figure 3.1, the CN imperfection-enhanced bond-energy deepens the atomic trapping potential well of the low-CN atom from \( E_b \) to \( E_i = c_i^{-m} E_b \) compared with the bulk value. Electrons surrounding the lower-CN atom are more localized in the relaxed surface region and hence contribute to the \( J_i \) of the lower-coordinated atom. If the localization probability is proportional to the well depth, then the densely localized electrons contribute to the \( J_i \) in the following way:

\[
\frac{J_i(z_i)}{J_b} \propto \frac{\mu_i(z_i)}{\mu_b} \propto \frac{E_i}{E_b} = c_i^{-m} \tag{4.3}
\]
CHAPTER 4 Physical Size Effect

The magnetic momentum in the direction of the applied field is $\mu_{iz} = J g_J \mu_B$, where $\mu_i(z_i)$ and $\mu_b$ represent the magnetic moment of an atom with $z_i$ at surface sites and an atom in the bulk situation, respectively. Note that the Lande’s $g$-factor ($g_J = 1.0$) is a function of the orbital and spin angular momentum, as shown in Eq (4.1), which is also affected by the CN imperfection. In the first-order approximation, this effect is neglected that may influence the precision of $m$ parameterization. As such, for an atom on a flat surface with $z_i = 4(c_1 = 0.88)$, the $\mu_i$ increases by $1-0.88^{-1} = 12\%$, which is similar to the cases of Fe-W, Fe-Fe, and Ni-Ni, where the interlayer distance contracts by 10-12%, which is associated with a 15–29% enhancement of the $\mu_i$. For a dimmer, $z_i = 2$, $c_i = 0.7$, the $\mu_i$ is enhanced by 40%, which agrees with the reported value of 3.2/2.22 for Fe, for example. If the effect of atomic CN imperfection and the pronounced portion of the lower-coordinated atoms in the nanosolid are taken into consideration, the magnetic properties of the ferromagnetic nanosolids should differ from those of the bulk.

For a spherical dot, $z_1 = 4(1 - 0.75/K_j)$, $z_2 = 6$, and $z_3 = 8$ for the first three surface layers worked sufficiently well in predicting the size dependence of a nanosolid. The mean angular momentum $J(K_j)$ of an atom in the nanosolid and its relative change can be obtained by:

$$N_i J(K_j) = N_i J + \sum_{i = 3}^{N_i} N_i (J_i - J)$$

$$J(K_j) - J = \sum_{i = 3}^{N_i} \frac{1}{c_i^{-m} - 1}$$

The $i$ is counted from the outermost layer to the center of the solid up to 3 as no CN imperfection is expected for $i > 3$. 

55
• Exchange energy weakening

The $M_S$ of the material is not only affected by the magnetic moment of an individual atom but also by the order of the spins, which depends on the vibrational energy and the exchange energy, $H_{ex}$, or the atomic cohesive energy, $E_{coh}$. The $H_{ex}$ can be expressed using the Ising model under a zero magnetic field:\(^{183}\)

$$H_{ex} = \sum_{\langle i,j \rangle} J_{ij} S_i \cdot S_j \propto z_i r_{ij}^{-m}$$

(4.5)

$S_i$ and $S_j$ are the spin operator, or the total angular momentum, of atoms in site $i$ and site $j$, respectively. $J_{ij} \propto r_{ij}^{-m}$ is the spin-spin exchange-coupling coefficient between the two sites. The $H_{ex}$ is a sum of $J_{ij}$ over all the possible $z_i$ of the considered atom.

The reduction of size affects the exchange energy in two aspects: (1) the increase of exchange energy for a single exchange bond caused by the bond contraction; (2) the reduction of the number of exchange bonds. Based on the BOLS mechanism, the size-induced change of the $H_{ex}$ is derived as:

$$\frac{H_{ex}(K_j) - H_{ex}(\infty)}{H_{ex}(\infty)} = \sum_{i,j}^N \frac{N_i}{N_j} \frac{z_i d_i^{-m} - z_b d_i^{-m}}{z_j d_j^{-m}}$$

$$= \sum_{i,j}^N N_j \sum_{b} y_i \left( \frac{z_i c_i^{-m}}{z_j c_j^{-m}} - 1 \right)$$

(4.6)

The interspin interaction controls the order of the spin system, which determines the $M_S$. At low temperatures, the magnetic moment (or total electronic spin) of the system may spontaneously change direction in a quantum tunneling process.\(^{173}\) At higher temperatures, the spin direction will fluctuate due to thermal agitation. Meanwhile, the magnitude of the magnetic moment
CHAPTER 4 Physical Size Effect

will decrease, and eventually vanishes at the Curie temperature \((T_C)\). The \(M_S\) of the system is determined by the sum over states of the spins, or the order of the spins. It is easy to understand that if one needs to disorder the spin-spin interaction by applying thermal stimulus, one has to provide sufficient energy to loosen all the bonds of the atom and to promote the atomic vibration. The exchange energy, or the exchange interaction, of a specific atom with \(z_i\) coordinates is the sum of all the bond energy, as given in Eq \((4.6)\).

- **Brillouin function – \(M_S(T, K_j)\)**

It is common to use the concept of “molecular field” to approach the spontaneous magnetization at \(T\) in terms of the Brillouin function, \(B_j(y)\), for a bulk.\(^{179}\)

\[
M(T) = g_j J \mu_B B_j(y)
\]

\[
B_j(y) = \frac{2J + 1}{2J} \coth \frac{2J + 1}{2J} y - \frac{1}{2J} \coth \frac{y}{2J} \quad (4.7)
\]

\[
y = \frac{J g_j \mu_B}{k_B T} H_m
\]

where \(J\) is the mean angular momentum and \(H_m\) is the molecular/crystal field. When the temperature \(T < 0.8T_C\), \(M_S(T) \approx M(T).\)\(^{179}\) The \(H_m\) is proportional to the exchange energy, \(H_m = AE_{exc}\), or the cohesive energy, where \(A\) is a constant. Therefore, replacing the mean \(J\) in a bulk with the size-dependent \(J(K_j)\), the temperature and size dependence of the \(M_S(K_j, T)\) is derived as:
where:

\[ E_{exc}(K_j) = E_{exc}(\infty) \left[ 1 + \sum_{i \in S} \gamma_i (c^{-m}_i - 1) \right] \]  

(4.9)

\[ J(K_j) = J \left[ 1 + \sum_{i \in S} r_i (c^{-m}_i - 1) \right] \]  

(4.10)

\( E_{exc}(K_j) \) and \( J(K_j) \) are the size-dependent exchange energy and the mean angular momentum of the nanosolid. Note that Eq (4.8) does not apply to an isolated atom without exchange interaction, though an isolated atom possesses intrinsic magnetic momentum.

The temperature and size dependence of \( M_S \) expressed as in Eq (4.8) is illustrated in Figure 4.1, where \( M_S \) is normalized by \( M_S(T = 0, K_j = \infty) \) and \( T \) is normalized by \( AE_{exc}(\infty) \). No oscillatory features are given as a smooth function in Eq (4.8) for the \( S/V \) ratio is used. The figure shows that, with the decrease in size, the \( M_S \) increases at low temperature while decreasing at high temperature, which indicates that at low temperature, the enhancement of the surface magnetic moment exhibits a dominant contribution for the \( M_S \), while at higher temperature, the reduction of exchange energy exhibits a dominant contribution for the \( M_S \). Note that Figure 4.1 shows only the \( M_S \) behavior of spherical dots of different \( K_j \). For those particles with more opening surface, especially for the
CHAPTER 4 Physical Size Effect

Figure 4.1 Counter plot of the BOLS predicted (see Eq (4.8)) \( M_S(T, K_j) \) for dot/particle, which shows that the \( M_S \) increases inversely with size at low temperature and decreases with size at mid-temperature. The \( M_S \) is normalized by \( M_S(T = 0, K_j = \infty) \) and \( T \) is normalized by \( A E_{exc}(\infty) \).

dimmer structure, the CN of surface atoms is much lower and the magnetic moment is therefore much higher than that shown here. As a result, the \( M_S \) at low T should be higher than the result shown in Figure 4.1.

4.1.2 \( T_C \) suppression

The Curie temperature is the temperature point at which the thermal vibrational energy overcomes the exchange energy. It is understandable that the total energy of a single bond is composed of two parts:

\[
E_{total}(d, T_C) = E_b(d) + E_V(T_C) = E_C
\]

(4.11)
The $E_b(d)$ is the binding energy at equilibrium atomic separation that is independent of the particular forms of the pair-wise interatomic potential. The $E_V(T)$ is the thermal vibrational energy. At the Curie point, the thermal vibration energy required to disorder the spin-spin exchange interaction is close to the exchange energy. Taking $E_{\text{total}}(d, T) = E_C$ as the reference point ($= 0$), we have:

$$E_b(d) + E_V(T_C) = 0$$  \hspace{1cm} (4.12)

Figure 4.2 illustrates the BOLS correlation mechanism for $T_C$ suppression. The separation between $E = 0$ and $E_C$ may vary from material to material, but it is constant for all bonds of a specific material. The distance between $E_C$ and the minimal bond energy at equilibrium atomic separation ($E_b(d)$, $E_b(d)$) determines the thermal energy that causes the order-disorder transition. Based on the mean field approximation and Einstein’s relation,\(^{86,184}\) Eq. (4.12) leads to

$$- J_{ij} \times S \times (S+1) + k_B T_C = 0,$$

and,

$$T_C \propto J_{ij} \propto d_i^{-1}$$  \hspace{1cm} (4.13)

where $S$ is the spin momentum. $J_{ij}$ relates to the inverse equilibrium atomic separation. The atomic cohesive energy is given as in equation (4.14):

$$E_{\text{coh},i} = \sum J_{ij} \propto z_i d_i^{-1}$$  \hspace{1cm} (4.14)

Considering the BOLS correlation in the surface region of a nanosolid containing a total atom number of $N_j$ with radius $R$, the total cohesive energy (exchange energy) of the entire nanosolid is the sum over all the atoms. A shell structure is used to incorporate the CN imperfection in the first three atomic layers:
Figure 4.2 The typical pair-wise potential for interatomic interaction. The BOLS correlation mechanism indicates that the bond length decreases with the CN of an atom at the surface with a response of a bond energy rise (in absolute value). The \( E(T_C) \) corresponds to the total energy at \( T_C \). The separation between \( E_b = 0 \) and \( E(T_C) \) is constant for all the bonds for a specific material and the separation between \( E_b(d) \) at the equilibrium atomic distance and \( E(T_C) \) is the thermal energy required to disorder the spin-spin interaction.\(^{158}\)

\[
E_{coh}(D) = N \sum_{i \leq j} N^i_j \left( z_i E_i - zE_b \right)
\]

(4.15)

where \( N_i \) is the atom number of the \( i \)-th surface layer, which contributes to the \( S/V \) ratio: \( \gamma = N_i/N_j \). The term \( N_j zE_b \) is the cohesive energy of the entire solid without the effect of CN imperfection being involved. The relative change of the cohesive energy of a nanosolid, or the mean value change of a single atom, follows:

\[
\frac{\Delta E_{coh}(R)}{E_{coh}(\infty)} = \sum_{i \leq j} N^i_j \left( z_i E_i - zE_b \right) = \sum_{i \leq j} \gamma_i \left( z_i c_i^{-1} - 1 \right)
\]

(4.16)
Eq. (4.16) indicates that the relative change of the cohesive energy of a nanosolid originates from the difference in the $E_{coh}$ between a surface atom and a bulk atom, $z_{ib}c_i^{-1} - 1$, due to the BOLS correlation. The trend of the change depends on the portion of surface atoms, $\gamma$, in the first three atomic layers with an appreciable degree of CN imperfection.

A calculation based on Eq (4.16) was carried out with the following parameters: $z_{ib} = 1/3$, $z_{2b} = 1/2$; $d_{Co} = 0.125$ nm, $d_{Fe} = 0.126$ nm, $d_{Ni} = 0.124$ nm. $T_{C,Fe}(\infty) = 1043$ K, $T_{C,Co}(\infty) = 1395$ K, $T_{C,Ni}(\infty) = 631$ K, respectively.

Figure 4.3 compares the predicted with the experimentally observed $T_C$ suppression of Fe, Co, and Ni thin films. Figure 4.4 shows the results for Fe$_2$O$_4$ nanoparticles. The model prediction matches well with the measurements. For ultra-thin films, the measured data are closer to the predicted curve for the spherical dot. This indicates that at the beginning of film growth, the films prefer to grow in an island pattern and transform gradually into a continuous plate. The slight difference between predictions and observations at small $K_j$ values can be minimized by adjusting the $c_1$ value. In the calculation, $z_{1b} = 1/3$ is used as a standard, corresponding to $c_1 = 0.88$. In fact, the $z_{ib}$ should decrease with the particle size as the curvature of the surface increases. On the other hand, the bond contraction coefficient also varies from source to source. For instance, the bond length between Ag, Cu, Ni, and Fe atoms and their neighbors were found to decrease with decreasing coordination. The bond lengths of the dimmer (2.53, 2.22, 2.15, and 2.02 Å, for Ag, Cu, Ni, and Fe, respectively) are shorter than the
Figure 4.3 Comparison of the predicted $T_C$ suppression (solid, dash and dot line) with observations (sporadic symbol) of (a) Ni thin films: data 1, data 2, 3, 4, data 5, data 6, and data 7; (b) Co films; and (c) Fe films.

Figure 4.4 Comparison of the predicted (solid and dash line) and the measured $T_C$ suppression of Fe$_3$O$_4$ nanoparticle (square symbol).
nearest-neighboring distance in their respective bulk values by 12.5% for Ag, 13.2% for Cu, 13.6% for Ni, and 18.6% for Fe. Therefore, a decrease of exchange energy at a surface has an enormous effect not only on the magnetization but also on the transition of a ferromagnetic nanosolid. It is our opinion that knowing the origin of the $T_C$ suppression is much more important than getting the precise fitting of the experimental data, which can easily be reached by adjusting the parameters.

### 4.2 Monte Carlo simulation

In order to examine the model consideration described above, MC simulation was carried out based on the BOLS-incorporated Ising convention. The enhanced surface magnetic moment was taken into consideration by varying the spin value, $S_i$, for each atom. Six kinds of nanosolids, as described in section 3.2.4, were considered in MC simulation to investigate the size, shape, and structure effect on the $M_S$ at various temperatures.

Figure 4.5 shows the MC-simulated $M_S(K_f, T)$ curves at zero applied magnetic field for (a) fcc dot, (b) fcc rod, (c) fcc plate, and (d) Icosahedra spin systems. The figures exhibit three outstanding regions with the increase in temperature. Generally, in the low-T region ($k_B T/J_{exc} < 3$), the $M_S$ increases when the solid size is reduced. In the mid-T region ($k_B T/J_{exc} \sim 6$), the $M_S$ drops with the solid size. At high T ($k_B T/J_{exc} > 9$), in the paramagnetic region, the residual $M_S$ increases as the size is reduced. These features are intrinsically common and depend less on the shape and structure of a specific solid. Figure 4.6 shows the
\( M_S(K_j, T) \) at \( k_B T/J_0 = 1, 6, \) and 12, which are the typical temperatures in the three regions.

### 4.2.1 \( M_S(K_j, T) \) enhancement at Low \( T \)

It can be seen from Figure 4.6 (a) that for a specific size, \( K_j \), the \( M_S \) of the fcc dot is higher than that of the fcc plate because an fcc dot has a higher \( \gamma_{ij} \) value than the fcc plate. In this region, the \( M_S \) increase inversely with size; the tendency is consistent with most of the experimental observations of size-induced enhancement of \( M_S \) at low temperatures.\(^{10,44,50,67,68}\) It is understood that when the temperature is very low, \( T \to 0 \) K, \( y \to \infty \), and then \( B_J(y) \to 1 \). Eq. (4.8) can then be approximated as: \( M_S(T \to 0) = NJ_B J \mu_B \cdot g_J \) and \( J \) follow Eqs (4.1) and (4.10), respectively. Using a shell structure in the BOLS correlation that calculates the magnetic moment of every atom layer by layer leads to the size-enhanced \( M_S \) for a nanosolid at very low temperature:

\[
\Delta M(K_j, T \to 0) = \frac{\sum_{\text{layer}} (c_i^{-m} - 1)}{M_b} 
\]

Agreement of MC simulations and BOLS calculations as well as the observed trends confirms the validity of the BOLS consideration that the \( M_S \) enhancement is dominated by the strongly localized electrons in the relaxed surface region.

### 4.2.2 \( M_S(K_j, T) \) tailoring at mid-\( T \)

In the second region, as shown in Figure 4.6 (b), the \( M_S(K_j, T) \) decreases with particle size in the vicinity of \( T_C \). In this region, the decrease of exchange energy overcomes the size effect on the surface magnetic moment. With the
increase of temperature, the thermal vibrational energy increases. The magnetization is hence not only affected by the individual magnetic moment of each atom but also by the order of the spins. The exchange energy of a small spin system is lower than that
Figure 4.5 MC-simulated temperature and size dependence of the $M_s$ for (a) fcc dot, (b) fcc rod, (c) fcc plate, and (d) Icosahedral spin systems.\textsuperscript{175}
CHAPTER 4 Physical Size Effect

of a larger spin system. As a result, in the small spin system, the number of nonaligned spins (minority) decreases. Correspondingly, the magnetization is smaller than that of the larger system.

Differentiating Eq (4.8) against $E_{exc}(K_j)$ leads to the $M_S(K, T)$ in the mid-T region:

$$\frac{\Delta M_S(K, T)}{M_S(\infty, T)} = \frac{E_{exc}(\infty)N_jg_J^2\mu_B^2A}{2k_BTMS(\infty, T)} \left\{ \text{csc} h^2 \left[ \frac{g_J\mu_B}{k_BT} AE_{exc}(\infty) \right] \right\} -$$

$$(2J+1)^2 \text{csc} h^2 \left[ \frac{(2J+1)g_J\mu_B}{2k_BT} AE_{exc}(\infty) \right] \times \frac{\Delta E_{exc}(K_j)}{E_{exc}(\infty)}$$

$$= \alpha(J, T)\sum_{i\in\Omega} \gamma_i (z_{ij}c_i^{-m} - 1)$$

(4.18)

where parameter $\alpha(J, T)$ is temperature and material dependent. At mid-temperature, the size effect on the $J$ becomes insignificant compared with the $E_{exc}$. Eq (4.18) indicates that the tailoring of $M_S$ at a temperature close to $T_C$ is dominated by the $E_{exc}$, which drops with solid size. The matching of predictions based on Eq (4.18) with $\alpha(J, T) = 1.4$ to the MC simulative results are shown in Figure 4.6 (b). The calculated trend is consistent with the measurement as well.

In the third region, at a temperature well above the $T_C$ of the largest particle, or in the paramagnetic phase, the remnant magnetism is higher for smaller particles, which is attributed to the slower temperature decay in the Monte Carlo study and to the increasing fluctuations with a decrease in the cluster size.31
CHAPTER 4 Physical Size Effect

Figure 4.6 The two outstanding regions showing the size-dependent $M_s(K_j, T)$ derived by MC simulation: (a) $k_B T/J_{exc} = 1$ (low-$T$); (b) $k_B T/J_{exc} = 6$ (mid-$T$) $|M|$ shift $= |M_s(K_j) - M_s(\infty)| / |M_s(\infty)| \times 100\%$.\textsuperscript{175}
CHAPTER 4 Physical Size Effect

Compared with the $M_S(K_j, T\sim0K)$ derived in Ref. [31] from the MC calculation, the current results show clear size dependence and the resonant features in region I, as experimentally observed by many researchers. The same trends of changes in regions II and III remain. In Ref. [31], the author assumed that even at very low temperature, the magnetization of a small particle is smaller than that of a large particle. The differences are due to the unawareness of the CN imperfection-enhanced atomic $\mu_i$ (or angular momentum $J(K_j)$) at that point of time. Without taking the enhanced surface $\mu_i$ into consideration, the magnetic moments for all the spins are equal, and the magnetization of the system is merely affected by the exchange energy and thermal vibrational energy. As a result, the enhancement of the magnetization at very low temperature for a nanosolid cannot be observed.

4.2.3 $M_S(K_j)$ oscillation and structural stability

Figure 4.7 (a) and (b) show the oscillation behavior of $M_S$ at smaller sizes, which is common to various crystal structures. This suggests that the oscillation originates from the $S/V$ ratio because some particles may have fewer surface atoms with a smaller $\gamma_j$ value than that of the adjacent larger or smaller particles. Figure 4.8 shows the $S/V$ ratio of the first surface layer of fcc and body-centered cubic (bcc) spherical dots, which can be compared with the $M_S$ behavior of the fcc spherical dot in Figure 4.7 (a). The behavior of the $S/V$ ratio versus the atom number has the same tendency. Therefore, it is not surprising that the fraction of the lower-coordinated surface atoms causes such artifacts. The simulative oscillation behavior is consistent with that observed in Ni clusters by Apsel et
who found an oscillation behavior and the smallest magnetic moments for clusters $N_{13}$, $N_{34}$, and $N_{55-56}$ at low temperatures.

Figure 4.7 Comparison of the size dependence of the $M_S$ of the fcc spherical particle, icosahedra, Marks decahedron (labeled as decahedron in the figure) and fcc truncated octahedron (labeled as octahedron in the figure) at temperature (a) $k_B T / J_{\text{exc}} = 1$ and (b) $k_B T / J_{\text{exc}} = 6$, showing the oscillation features and the structural stability. Lower $M_S$ at low $T$ indicates that fewer atoms are located at the surface, corresponding to a more stable structure.\textsuperscript{175}
The physical properties of nanosolids in a molecular regime typically exhibit a very irregular dependence on their aggregate size, with certain sizes standing out in particular, namely “magic numbers.” In a mesoscale regime, on the other hand, they behave in a regular way. As can be seen, compared to other structures, the icosahedron, the Marks decahedron, and the fcc truncated octahedron have lower $M_S$ in the low-$T$ region and higher $M_S$ in the mid-$T$ region, especially the small icosahedral particles $N_{55}$ and $N_{147}$. The mass spectra of nanosolids usually exhibit especially abundant sizes that often reflect particularly stable structures, especially reactive nanosolids, or closed electronic shells. These “magic number” sizes are of great theoretical interest since many of them correspond to compact structures that are especially stable. The magnetic moment of ferromagnetic nanosolids has been reported to exhibit the same behavior. The simulative results in this study show the same cases that $N_{13}$, $N_{55}$, and $N_{147}$ are the magnetic number for small magnetic nanoparticles.

![Figure 4.8](image.png)

Figure 4.8 Shows the quantized S/V ratio $\gamma$ of the first surface layer of fcc and bcc structures.\textsuperscript{175}
CHAPTER 4 Physical Size Effect

confirming that the icosahedron is the most closed structure for small size.

However, when the atom number, $N_j$, is larger than 300, the fcc truncated octahedron exhibits the smallest $M_S$ in the low-T region and the highest $M_S$ in the mid-T region, indicating that it is the most compact structure when $N_j > 300$. The MC simulation results here are consistent with a recent experimental study on copper particles, in which Reinhard et al.\textsuperscript{187} showed that the icosahedral structure dominates at sizes well below a diameter of 3.8 nm, while the fcc structure is preferred at this size or above. This arises from the energy competition between reducing the surface energy and increasing the strain energy. It often happens that icosahedra are the most stable at small sizes due to their low surface energy and good quasispherical structures, decahedra are favorable at intermediate sizes, and crystalline structures are preferred in the limit of large objects.

4.2.4 $T_C$ suppression

The drop of exchange energy also determines the critical temperature of the melting and phase transition:

\[
\frac{\Delta E_{\text{exc}}(K)}{E_{\text{exc}}(\infty)} = \frac{\Delta T_C(K)}{T_C(\infty)} = \frac{\Delta T_m(K)}{T_m(\infty)} = \sum_{i=3}^{\infty} \gamma_i z_i c_i^{-m} - 1 \quad (4.19)
\]

The MC simulation also shows the $T_C$ suppression, which is consistent with the BOLS predictions that have been discussed in detail in section 4.1.2. The BOLS predictive and simulative results are shown in Figure 4.9. When $K = 3.9$, $T_C$ suppression of the films is about -40%. The bulk value of $kT_C/J_0 \approx 13$ is used during the normalization.
CHAPTER 4 Physical Size Effect

4.3 Experimental verification

- Magnetization

To investigate the size effect on the magnetization of the thin film, Ni films were deposited by the FCVA technique (100 ~ 124 nm). The grain size ranged from 3 to 10 nm. Figure 4.10 shows the typical 3D AFM morphology of the Ni film with roughness (RMS) of 0.8 nm. XRD profiles in Figure 4.11 show three strong peaks corresponding to the Ni(111), Ni(200), and Ni(220) faces. The two resolved small peaks belong to the silicon. The XRD profile for the bare silicon substrate was compared; the shift of Si peaks was due to the different rotation angle of silicon substrates in the plane of the sample holder. The stronger and sharper nickel peaks indicated a larger grain size according to Scherrer’s equation. The grain sizes derived from the Scherrer equation were about 3.1, 3.2, 5.5, 7.9, and 10.0 nm.

Figure 4.9 The size dependence of $T_C$ shift by MC simulation together with the BOLS prediction.
Figure 4.10 The typical surface morphology of Ni thin film deposited on silicon substrate using FCVA. The surface is smooth with a roughness (RMS) of about 0.8 nm.

Figure 4.11 X-ray diffraction pattern of the Ni film at various substrate temperatures. The peak intensity decreases and the peaks become broader with the decrease of the substrate temperature, indicating a decrease in crystalline size.
Figure 4.12 shows the magnetization-hysteresis (M-H) loops of Ni films measured at room temperature, note that H=0 should be in the center of the loops, the shift of the loop is due to the reading shift of VSM. With the reduction in the grain size, the squareness and saturation magnetization decrease while the coercivity (H_C) increases. The size dependence of the M_S tailoring at room temperature is shown in Figure 4.13. The M_S drops with particle size, K_j = D / 2d, where d = 0.2488 nm is the diameter of the Ni atom and D is the diameter of the grain size. The M_S tailoring of films with K_j ≈ 6 is about -83% compared with the bulk value (6.068 kG). Even for the film with K_j = 20, the M_S decreases by 31% compared with the bulk value. Theoretical fitting with α(J, T) = 4.0 from Eq (4.18) is also shown in Figure 4.13. The tendency of the size dependence of M_S is consistent with most of the experimental observations^67-72 and agrees with the Monte Carlo simulations in region II. The dash line is the M_S prediction at a lower temperature with α(J, T) = 1.6, which shows a higher M_S with the same size. It is interesting that when the particle size is reduced to K_j = 5 (D = 2.5 nm), M_S = 0. This means the Curie temperature decreases to near room temperature when K_j reaches 5. For an Ni particle of K_j = 5, the T_C drops by ~51% from 631 K to 309 K.\(^{188}\) While at low temperature with α(J, T) = 1.6, the M_S still remain around half of the bulk value.

One may wonder about the effect of impurities such as surface oxidation on the measurement. Although XRD and XPS revealed no impurities in the samples, we cannot exclude the existence of trace impurities. However, all the samples were prepared and measured under the same conditions and we used the relative change of the quantities, which should minimize the influence of such artifacts.
CHAPTER 4 Physical Size Effect

caused by impurities whether they exist or not, and the measured data should be purely size dependent.

Figure 4.12 Size dependence of the M-H loops of Ni films.\textsuperscript{188}

Figure 4.13 Crystalline size dependence of $M_S$ under the maximum applied of 10 k Oe at ambient. The tendency agrees with most of the experiment observations and the Monte Carlo calculations in region II. The solid line and dot line are the theoretical prediction based on Eq. (4.18) with $\alpha(T) = 4.0$ and lower temperature $\alpha(T) = 1.6$ respectively.\textsuperscript{188}
CHAPTER 4 Physical Size Effect

- Coercivity

Generally, in ferro- or ferrimagnets, magnetic particles consist of magnetic domains if the particle diameter exceeds several hundred nanometers.\(^ {189}\) In contrast, when the particle size decreases to tens of nanometer, the particles become a single magnetic domain. In that case, the magnetization process also changes from the domain-wall motion to a whole-spin rotation in the magnetic particle. Because the whole-spin rotation requires more energy than the domain-wall motion, it is hard to magnetize a single magnetic domain particle.\(^ {190}\)

It is known that both the interspin interaction within a domain \((E_{\text{exc}})\) and the intergrain interaction within a solid \((E_{\text{EXC}})\) composed of nanograins can be described using the Ising model. Considering a grain as a giant spinner, with a magnetic moment \(S\), the exchange energy of the spinner interacting with its \(z_i\) nearest neighbors follows the Ising model, as shown in Eq (4.5). For intergrain interaction, the \(d_i\) is replaced with grain diameter, \(D\), if a uniform grain size is assumed. The \(z_i\) is the number of neighboring grains of a specific grain. \(S_i\) and \(S_j\) are giant spins for a grain. For an isolated grain below a certain size (of the order of 15 nm, i.e. about \(10^5\) atoms per Fe cluster\(^ {191}\)), for an isolated grain below a certain size, the coercivity is zero (superparamagnetic), considering a grain as a giant spin, when may grains get closer, the intergrains’ exchange energy increases, which dominates the anisotropy energy.\(^ {94}\)

\[
H_c \propto \frac{1}{2} H_S \propto E_{\text{EXC},i} \propto ZD^{-1} \tag{4.20}
\]
CHAPTER 4 Physical Size Effect

where $H_S$ is the field to uniformly rotate the moments into alignment that is proportional to the intergrain interaction. $Z$ is the mean effective number of neighboring grains of the specific grain.

Figure 4.14 shows the measured grain size dependence of the coercivity together with the theoretical prediction. The prediction in Eq (4.20) fits well with the measured $H_C$ with $m = 1$. The bulk value is 0.7 Oe. The size-enhanced $H_C$ is consistent with other observations of soft magnetic materials such as Fe-Ni films\textsuperscript{192} and Co-Fe-Ni films\textsuperscript{193}.

- Other properties

*Squareness:* The M-H loop provides information about the squareness. The squareness factor is defined by the ratio of the reverse field required to reduce

![Figure 4.14 Size-enhanced $H_C$ characterized at room temperature.](image)

Figure 4.14 Size-enhanced $H_C$ characterized at room temperature.
magnetization by 10% from the remanence to $H_C$. A squareness factor of 1 corresponds to a perfectly square loop. Another parameter that represents the squareness is the remanence ratio, $R_r$, which is defined as $R_r = M_r / M_S$. The loop shifts due to the zero position shifts of VSM. To find the $M_r$, it is needed to re-center the loops along the x-axis to get an equal $H_c$ on both side of y-axis. Figure 4.15 shows the squareness factor and the remanence ratio as a function of size. The squareness factor decreases with grain size.

**Permeability:** The permeability ($\chi_m$) was found to decrease with the decrease in size, which is consistent with the grain boundary model (NMGB)\textsuperscript{101} as introduced in section 2.1.3. The grain size effects on the magnetic properties of Ni films are summarized in Table 4.1.

**Anisotropy:** The ferromagnetic thin films normally show two distinguishing magnetizations along and perpendicular to the film’s surface.

![Figure 4.15](image_url)  

**Figure 4.15** The squareness factor and remanence ratio as a function of size.
### Table 4.1 Size effect on the in plane magnetic properties of Ni films.

<table>
<thead>
<tr>
<th>Grain size (nm)</th>
<th>$4\pi M_S$ (kG)</th>
<th>$4\pi M_r$ (kG)</th>
<th>$H_{Cm}$ (kOe)</th>
<th>Squareness</th>
<th>$R_r$</th>
<th>$\chi_m$</th>
<th>$\mu/\mu_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>6.08</td>
<td>/</td>
<td>0.0007</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>0.6</td>
</tr>
<tr>
<td>10.0</td>
<td>4.2</td>
<td>3.9</td>
<td>0.078</td>
<td>0.57</td>
<td>0.93</td>
<td>25.88</td>
<td>0.41</td>
</tr>
<tr>
<td>7.9</td>
<td>2.6</td>
<td>2.1</td>
<td>0.135</td>
<td>0.20</td>
<td>0.81</td>
<td>5.59</td>
<td>0.26</td>
</tr>
<tr>
<td>5.5</td>
<td>3.5</td>
<td>2.6</td>
<td>0.12</td>
<td>0.19</td>
<td>0.74</td>
<td>7.70</td>
<td>0.34</td>
</tr>
<tr>
<td>3.2</td>
<td>1.05</td>
<td>0.35</td>
<td>0.27</td>
<td>0.064</td>
<td>0.33</td>
<td>1.16</td>
<td>0.10</td>
</tr>
<tr>
<td>3.1</td>
<td>1.35</td>
<td>0.35</td>
<td>0.21</td>
<td>0.050</td>
<td>0.26</td>
<td>0.69</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Figure 4.16 compares the M-H loops for a field applied parallel (//) and perpendicular (⊥) to the film’s surface. It can be seen that the easy magnetization direction is parallel to the film’s surface. When the field is applied perpendicular to the film’s surface, the remanence and squareness are much lower and the coercivity is much higher.

![M-H loops](image)

Figure 4.16 M-H loops of Ni films 148 nm thick under field applied to the direction parallel (//) and perpendicular (⊥) of the surface plane.
CHAPTER 5 RESULTS AND DISCUSSION II:

NITROGEN-CATALYTIC EFFECT

5.1 BBB perdition

In the previous section, we discussed that miniaturization of a ferromagnetic solid can modify the magnetization by reducing the exchange energy and increasing the surface spin magnetic moment in the Ising model. This section shows that the chemical reaction of iron with nitrogen also modifies the magnetization by changing the angular momentum of the ferromagnetic atoms.

5.1.1 Ms

Figure 5.1 illustrates the BBB bond model for a nitride (NB₃). A nitrogen atom hybridizes and interacts with an arbitrary element, B, through four directional orbitals to form a quasitetrahedron. Atoms labeled 1 are B⁺; atoms labeled 2 are lone-pair induced B dipoles with an expansion in size and elevations of energy states. When a reaction takes place, all atoms change their sizes and valence states. The N-B bonds are mainly ionic or polar-covalent due to the difference in electronegativity (χ) between N and B, (χ₇ = 3.0, χₓ < 2.5, for metal and semiconductor χₓ = 1.5-1.9). Formation of the nonbonding lone pair is the intrinsic feature of N and it is independent of element B being considered. However, the number of lone pairs determines the C₃ group symmetry of NB₃, and consequently, some physical properties. The symmetry may change depending on the bonding circumstance. 196,197,198
Figure 5.1 The BBB model for nitridation. N hybridizes and interacts with arbitrary element B through the bonding and nonbonding lone pair to form the quasitetrahedron: NB$_3$ [N$^3$ + 3B$^{+1}$ (labeled 1) + B (dipole, labeled 2)]. The number and orientation of the lone pair give different geometrical symmetry as indicated.$^{194}$

When a small amount of nitrogen is added into the Fe lattice, the energy band of Fe is modified.$^{194}$ Alternation of the Fe valences changes the magnetic moments of the Fe atoms in different ways according to Hund’s law, as shown in Figure 5.2 for the possible atomic valence states. The reaction alters the atomic states of iron from Fe (3d$^6$4s$^2$, J = 2.22) to Fe$^+$ (3d$^5$4s$^2$, J = 2.50) or Fe dipole (3d$^5$4s$^2$4p$^1$, J = 4.0, or even 3d$^5$2s$^2$4d$^1$, J = 5.0). In the former, Fe donates one 3d electron to the sp$^3$-hybrid orbital of N, while in the latter, one 3d electron jumps into the Fe’s outer empty shells, 4p or 4d, with higher energy. For a (N$^3$ + 3Fe$^{+1}$ + Fe (dipole)) cluster, the average J enhances from 2.22 (measurement) to 2.875 or even 3.125.$^{194}$ The possible atomic valence states and the corresponding angular momentum of an iron atom and its ions are shown in Table 5.1.
CHAPTER 5 Nitrogen-catalytic Effect

<table>
<thead>
<tr>
<th>VALENCE STATE</th>
<th>CONFIGURATION</th>
<th>S = ΣS_j</th>
<th>L = ΣL_j</th>
<th>J=(L±S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>3d⁶4s²</td>
<td>2(=4×1/2)</td>
<td>0(3d-frozen)</td>
<td>2(2.22)</td>
</tr>
<tr>
<td>Fe⁺</td>
<td>3d⁵4s²</td>
<td>2.5</td>
<td>0</td>
<td>2.5</td>
</tr>
<tr>
<td>Fe⁺²</td>
<td>3d⁵4s¹</td>
<td>2.5+0.5</td>
<td>0</td>
<td>3.0</td>
</tr>
<tr>
<td>Fe(dipole 1)</td>
<td>3d⁵4s²4p¹</td>
<td>2.5+0.5</td>
<td>0+1</td>
<td>4.0</td>
</tr>
<tr>
<td>Fe(dipole 2)</td>
<td>3d⁵4s²4d¹</td>
<td>2.5+0.5</td>
<td>0+2</td>
<td>5.0</td>
</tr>
</tbody>
</table>

As an approximation, considering an Fe system of y atoms, with x nitrogen atoms introduced into the Fe lattice, the percentage of nitrogen is \( a_N = \frac{x}{(x + y)} \) × 100%. Suppose every nitrogen atom changes the valence states of its four neighboring Fe atoms from 4Fe to N³⁻ + 3Fe⁺¹ + Fe (dipole), the average magnetic moment of its four neighboring iron atoms then changes from 2.22 to 3.125. For an iron nitride system with N:Fe < 1 : 4, the average magnetic moment of the whole system can be approximately estimated as:

\[
\bar{\mu} = \mu \times \frac{4x \times 3.125 \mu_B + (y - 4x) \times 2.2 \mu_B}{y} = 2.2 \mu_B + \frac{3.7x}{y} \mu_B \tag{5.1}
\]

The relative change can then be expressed as:
which shows that the magnetic moment of the iron system increases with the percentage of nitrogen. However, Eq. (5.2) only applies when the nitrogen content is low (N : Fe < 1 : 4). With an increase in the nitrogen in the films, the degree of polarization for Fe$^{\text{dipole}}$ will decrease. The dipole electron may even be captured by the excess nitrogen atom and form a valence state, Fe$^+$, with a lower magnetic moment than that of the Fe$^{\text{dipole}}$. As a result, the $4\pi M_S$ will decrease. The experimental result shows that when the $a_N > 0.107$ (N: Fe $\approx$ 3 : 25), the $4\pi M_S$ begins to decrease, indicating that the formation of a hydrogen bond like that will decrease the momentum of the Fe specimen. The tendency of the BBB predictions is consistent with the electronic structure calculations.\textsuperscript{199}

Most of the calculations use the local spin density approximation, many use the atomic spheres approximation, and some use the first-principles calculations. The calculated Fe electron structure indicates that the nearest neighbors of the nitrogen atom have a reduced spin splitting, while the more distant iron shows a deeper spin splitting (Fe dipoles), which increases the magnetic moment compared with the pure iron.\textsuperscript{199}

### 5.1.2 Resistivity

The alteration of the atomic states of iron from Fe to Fe$^+$ or Fe dipole also change the resistivity of the material. As indicated in Figure 5.1, nitrogen interacts with atoms of iron and hybridizes its $sp$ orbitals to form four directional orbitals. Nitrogen captures three electrons from iron atoms, and the 2s and 2p levels of nitrogen are fully occupied with eight electrons that will
repopulate in the four directional orbitals. Therefore, three of the four hybridized orbitals are occupied by shared electron pairs (bonding orbitals). The remaining orbital is occupied by the lone electron pair of nitrogen (nonbonding orbitals).

The formation of bonds, nonbonding lone pair, and antibonding dipoles, as well as the H-like bonds, generates corresponding features that add to the DOS of the valence band and above of the host. The electrons are then more localized and hence the carrier mobility is lower. The additional DOS features of bonding $\ll$ Fermi energy ($E_F$), holes $\leq E_F$, and antibonding dipoles $\leq E_F$. With the full occupancy of the p-orbital of nitrogen, the $sp$ orbitals of the nitrogen hybridize. As a result, electronic vacancies are produced right below $E_F$, generating a gap between the conduction band and the valence band of Fe. Consequently, with the nitrogen catalysis, the resistivity increases.

### 5.2 Deposition of Fe-N films

The deposition conditions are summarized in Table 3.3. Three approaches have been used to introduce nitrogen into the films, as described in section 3.3.3. In approach I, it was found that even when the nitrogen partial pressure was increased up to $2.0 \times 10^{-4}$ torr, it was hard to detect nitrogen in the films. Therefore, this approach is less effective. In approach II, nitrogen was incorporated into the films. The nitrogen concentration in the film can be controlled by changing the nitrogen partial pressure, $P_N$. This approach limits the nitrogen concentration in the film. In order to further increase the nitrogen concentration, approach III was implemented.
5.2.1 Deposition rate

Both the approaches and the gas pressure significantly affect the deposition rate, \( R \). Figure 5.3 (a) shows the dependence of the deposition rate on the \( P_N \) in approach II. The deposition rate decreases from 39 nm/min to 15 nm/min when the \( P_N \) increases from \( 7 \times 10^{-5} \) torr to \( 2.0 \times 10^{-4} \) torr. Increasing \( P_N \) results in an increase in the frequency of collision between the ions and the nitrogen molecules; correspondingly, the mean free path, the energy of ion, and the plasma density decrease. As a result, the deposition rate decreases.

Figure 5.3 (b) shows the deposition rate that is affected by the \( P_N:P_{Ar} \) ratio in approach III. The deposition rate is affected significantly by the \( P_N:P_{Ar} \) ratio. The highest deposition rate in approach III is 6.4 nm/min, which is much smaller than that in approach II. When the \( P_N:P_{Ar} = 10:7 \), the deposition rate decreases to 0.35 nm/min, which indicates that the resputtering effect of \( Ar^+ \) becomes significant when the Ar ratio is high.

![Figure 5.3](image)

Figure 5.3 The deposition rate \( R \) varies (a) with \( P_N \) in approach II and (b) \( P_N:P_{Ar} \) in approach III.
5.2.2 Surface morphology

The surface morphology differs greatly between the films deposited using different approaches. Figure 5.4 (a) and (b) shows that the films deposited using approach II possess a smooth surface morphology. The RMS (<0.3 nm) of the films deposited using approach II is much lower than that of the films deposited using approach III (~1.5 nm), as shown in Figure 5.4 (c) and (d). This is because the bombardment of the energetic ion beams in approach III is more severe than that in approach II due to the introduction of an ion beam source.

![Typical AFM surface morphology of the Fe-N films deposited using approaches II and III.](image)

Figure 5.4 Typical AFM surface morphology of the Fe-N films deposited using approaches II and III. With an RMS value of about 0.3 nm, the films using approach II are far smoother than those with an RMS about 1.6 nm deposited using approach III. The films thickness is 75 ± 5 nm.
CHAPTER 5 Nitrogen-catalytic Effect

5.2.3 Microstructure

The XRD patterns of sample II-1 and II-4 are shown in Figure 5.5 (a). Sample II-1 consists of $\alpha + \alpha' + \alpha'' + \gamma'$ multiphases, while sample II-4 possesses nitrogen-poor phases ($\alpha + \alpha'$) due to the lower $P_N$. This is because the higher pressure of $N_2$ results in higher nitrogen ionization in the plasma area, which introduces a higher nitrogen ion dose in the plasma. Accordingly, the nitrogen concentration in the films is higher. Figure 5.5 (b) shows the XRD pattern of sample III-1 that was deposited with $P_N:P_{Ar} = 100:7$ using approach III. The pattern exhibits a clear $\gamma''$-FeN phase. When $P_N:P_{Ar}$ is reduced to 80:7, multiphases including $\gamma$, $\zeta$, and $\epsilon$ are exhibited in the Fe-N films, as shown in Figure 5.5 (c). With a further decrease in the $P_N:P_{Ar}$, all the samples exhibit a single $\zeta$-Fe$_2$N phase, as shown in Figure 5.5 (d) and (e). Decreasing the $P_N:P_{Ar}$ ratio in the ion beam source increases the bombarding and etching effect of $Ar^+$. As a result, a smaller grain size, poor crystallinity, and lower nitrogen concentration were obtained. When the $P_N:P_{Ar}$ decreases to 20:7 and 10:7, as shown in Figure 5.5 (f), only weak $\alpha$ and $\alpha'$ peaks are observed.

5.2.4 Binding energy

Figure 5.6 shows the XPS profiles for the samples of pure Fe, II-1, III-1, III-3, and III-6. The Fe 2p XPS peak is around 707.0 eV$^{37,200}$, while the peaks at about 711 eV or higher in XPS Fe 2p$^{3/2}$ spectra for samples III-1, III-3, and III-6 are related to Fe$^{2+}$ and Fe$^{3+}$ contribution.$^{201,202,203}$ The peaks of Fe 2p$^{3/2}$ are significantly strong in sample III-1, which indicates that the proportion of Fe$^{2+}$/Fe$^{3+}$ to Fe is larger; in other words, the nitrogen concentration is higher in the sample. This can be confirmed in the N1s spectra as well.
Figure 5.5 XRD profiles of the Fe-N films. (a) II-1 ($P_\text{N} = 2.0 \times 10^{-4}$ torr) & II-4 ($P_\text{N} = 0.7 \times 10^{-4}$ torr) show nitrogen-poor phases. (b) III-1 ($P_\text{N}:P_\text{Ar} = 100:7$) exhibits $\gamma''$-FeN phase. (c) II-2 ($P_\text{N}:P_\text{Ar} = 80:7$) presents $\epsilon$ and $\gamma''$ phases. (d) III-3 ($P_\text{N}:P_\text{Ar} = 40:7$) and (e) III-4 ($P_\text{N}:P_\text{Ar} = 50:7$) show $\zeta$-Fe$_2$N phase. Only weak $\alpha$ and $\alpha'$ peaks can be observed in (f) III-6 and III-7 ($P_\text{N}:P_\text{Ar} = 20:7$ and 10:7 respectively). (films thickness: $75 \pm 5$ nm)
Figure 5.6 XPS binding energy of Fe, III-1, III-4, III-6, and II-1. The intensity of peak 707 decreases while peak 711 increases, which indicates the number increase of Fe$^{2+}$ and Fe$^{3+}$.

The XPS N1s spectra for samples II-1, III-1, III-3, and III-6 in Figure 5.7 show a pronounced peak at 397 eV that corresponds to the typical Fe-N bond. A small shift can be resolved in III-1, indicating a stronger Fe-N bonding state in sample II-1 than in sample III-1. The intensities of the N1s peaks of samples III-1, III-3, and III-6 are larger than those of sample II-1, which indicates that the nitrogen concentration in these samples is higher than that in sample II-1. This is because with the assistance of the ion beam source, nitrogen is easier to be incorporated into the films. The nitrogen concentrations that were calculated based on the N1s peaks are shown in Table 5.2.
5.3 Nitrogen catalytic effect

5.3.1 $M_S$

Figure 5.8 (a) shows the in-plane M-H loops of the films deposited using approach II (samples II-1 to II-4) in comparison with the nitrogen-free iron film. The $4\pi M_S$ value of the pure Fe films is about 8.8 kG, which is much lower than the bulk value, 21.5 kG. This originated from the suppression effect of size reduction as discussed in section 4.1. Figure 5.8 (b) shows the in-plane M-H loops of the films deposited using approach III. The magnetization and squareness are smaller than those of the films deposited with method II. Figure 5.9 shows the $4\pi M_S$ versus the nitrogen concentration. With the increase in the nitrogen concentration, the $4\pi M_S$
firstly increases and then decreases. The highest $M_S$ is exhibited in the II-3 sample with a nitrogen concentration of $a_N \approx 10\%$ and with multiphases of $\alpha$ and $\alpha'$, which is even higher than that of the bulk Fe. When $a_N = 10\%$, the corresponding enhancement of $4\pi M_S$ calculated by Eq (5.2) is 20\%. This value is higher than that observed here (14.0\%), which is due to the physical size-induced suppression of $4\pi M_S$ at ambient, as discussed in section 4.1.1.
Figure 5.9 The $4\pi M_S$ of the films with different nitrogen concentration. The $4\pi M_S$ of the nitrogen-poor films are higher than those of the pure Fe film, while the $4\pi M_S$ of the nitrogen-rich films are lower.

With a further increase in the nitrogen concentration, nitrogen-rich phases such as $\varepsilon$ and $\gamma''$ appear, and the $4\pi M_S$ decreases to a value that is even below that of the pure iron thin films. For sample III-1, which only exhibits $\gamma''$ phase in the XRD profiles, the $4\pi M_S$ is close to zero. This is consistent with the findings in regard to the Fe-N magnetic properties by Jiang et al\textsuperscript{120} as well as with our theoretical prediction based on BBB correlation as described in section 5.1.

The nitrogen catalytic effect on the $M_S$ can be summarized as follows:

1. Poor nitrogen concentration enhances the $M_S$ of iron films due to the change of the valance state.
(2) The $M_S$ of the pure iron film is lower than the bulk value, which is consistent with the study on Ni thin films and the theoretical prediction for the size effect on the $M_S$ of nanosolids as discussed in section 4.1.

(3) The physical size effect causes a drop in the $M_S$ of a nanosolid. In contrast, the nitrogen catalytic effect enhances the $M_S$ at low nitrogen concentration. In the thin iron films with low nitrogen concentration, joint effects of the size and nitrogen catalysis occur and the nitrogen catalytic effect becomes dominant. As a result, the $M_S$ is enhanced to a level even higher than the bulk Fe value.

(4) If too much nitrogen is added to the iron films, the $M_S$ decreases due to the decrease in the number of Fe$^{\text{dipole}}$, the formation of an H-bond-like formation, and the formation of different types of lattice with smaller exchange strength.

### 5.3.2 Coercivity and squareness

The $H_C$ of the films is shown in Figure 5.10. With oscillations, the $H_C$ tends to decrease slightly with the increase in the nitrogen concentration. Other properties such as the squareness and the remanence have no apparent dependence on the nitrogen concentration. The nitridation effects on the magnetic properties of iron films are summarized in Table 5.2.

### 5.3.3 Resistivity

Figure 5.11 shows the resistivity of Fe-N films as a function of the nitrogen concentration, measured using a four-point probe measuring system. With an
Figure 5.10 The nitrogen concentration dependence of the $H_C$ of the Fe-N films. $H_C$ tends to decrease with oscillation behavior when nitrogen increases.

Table 5.2 Summary of the magnetic properties of Fe-N films. $^{178}$

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Phases</th>
<th>Nitrogen concentration $a_N$ (%)</th>
<th>$4\pi M_S$ (kG)</th>
<th>$4\pi M_r$ (kG)</th>
<th>$H_{Cm}$ (kOe)</th>
<th>$R_r$</th>
<th>$\mu$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>$\alpha$</td>
<td>0.0</td>
<td>8.8</td>
<td>8.5</td>
<td>0.15</td>
<td>0.97</td>
<td>0.9</td>
</tr>
<tr>
<td>II-1</td>
<td>$\alpha + \alpha'' + \gamma'$</td>
<td>0.16</td>
<td>13.5</td>
<td>13.1</td>
<td>0.11</td>
<td>0.97</td>
<td>-</td>
</tr>
<tr>
<td>II-2</td>
<td>$\alpha + \alpha'$</td>
<td>0.13</td>
<td>11.8</td>
<td>10.4</td>
<td>0.10</td>
<td>0.88</td>
<td>-</td>
</tr>
<tr>
<td>II-3</td>
<td>$\alpha + \alpha'$</td>
<td>0.10</td>
<td>24.5</td>
<td>15.3</td>
<td>0.23</td>
<td>0.62</td>
<td>2.5</td>
</tr>
<tr>
<td>II-4</td>
<td>$\alpha + \alpha'$</td>
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<td>15.4</td>
<td>13.5</td>
<td>0.13</td>
<td>0.88</td>
<td>1.6</td>
</tr>
<tr>
<td>III-1</td>
<td>$\gamma''$</td>
<td>0.49</td>
<td>0.223</td>
<td>0.041</td>
<td>-</td>
<td>0.18</td>
<td>-</td>
</tr>
<tr>
<td>III-2</td>
<td>$\gamma'' + \zeta + \epsilon$</td>
<td>0.45</td>
<td>0.896</td>
<td>0.229</td>
<td>0.07</td>
<td>0.26</td>
<td>0.15</td>
</tr>
<tr>
<td>III-3</td>
<td>$\zeta$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>III-4</td>
<td>$\zeta$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>III-5</td>
<td>$\zeta$</td>
<td>0.33</td>
<td>2.286</td>
<td>1.27</td>
<td>0.124</td>
<td>0.56</td>
<td>-</td>
</tr>
<tr>
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<td>3.628</td>
<td>1.136</td>
<td>0.067</td>
<td>0.31</td>
<td>0.4</td>
</tr>
<tr>
<td>III-7</td>
<td>$\alpha + \alpha''$</td>
<td>0.19</td>
<td>5.253</td>
<td>2.519</td>
<td>0.064</td>
<td>0.10</td>
<td>0.6</td>
</tr>
</tbody>
</table>
increase of the nitrogen concentration, the resistivity of the films increases exponentially, which confirms the localization of the electrons and the formation of a band gap when nitrogen was introduced, as was discussed in section 5.1.2.

### 5.4 Extension: bias effect

The high ionization facilitates the control of the ion energy by biasing the substrate, which has a strong influence on the surface morphology and the microstructure of the coating.\(^ {204,205} \) Hence, in the case of the FCVA technique, the bias voltage is an important parameter. This section describes the study of...
the bias effect on the surface morphology, microstructure, and magnetic properties of the Fe-N films. The deposition details are given in section 3.3.3.

5.4.1 Deposition rate and surface morphology

The deposition rate was apparently affected by the bias voltages. At a floating potential, the deposition rate was 16.4 nm/min, but when the bias voltages were increased up to –50, –100, and –400 V, the deposition rates decreased to 16.0, 14.7, and 5.1 nm/min, respectively. The reduction of deposition rates with the increase in bias voltages indicates that the resputtering effect on the film surface is becoming intense due to the increase of ion energy. This is especially obvious in the deposition at a bias voltage of –400 V, which has a deposition rate only 31% of that at a floating potential.

The surface morphologies also change with the bias voltage. Figure 5.12 shows the AFM images of the films deposited at different substrate biases. As the bias voltage increased from 0 to –50 V, the surface remained smooth. With a further increase in bias voltage, the surface became roughened, indicating a significant coarsening of the film structure. The film deposited at a bias voltage of –100 V exhibited spherical-like clusters with a size of 15~40 nm. When deposited at a bias voltage of –400 V, the film possessed a cluster around 50 nm in size due to the coalescence. Figure 5.13 shows the influence of the bias voltage on the RMS of the films, calculated from the AFM image over an area of 500 nm × 500 nm. The roughness value first decreased to its lowest value of 0.14 nm with an increase of the bias voltage to –50 V, and then increased rapidly as the bias voltage increased up to –400 V.
CHAPTER 5 Nitrogen-catalytic Effect

Figure 5.12 AFM images of the films deposited at various bias voltages.

Figure 5.13 Bias dependence of surface roughness (RMS). The film deposited at –50 V bias voltage exhibits the lowest RMS value.
CHAPTER 5 Nitrogen-catalytic Effect

5.4.2 Microstructure

The XRD profiles in Figure 5.14 show three peaks at 44.3°, 64.6°, and 82.2°, corresponding to (110), (200), and (112) planes of α-Fe(N), respectively. According to the JCPDS-International diffraction database, the first three strongest peaks for pure α-Fe are at 44.8°, 65.2°, and 82.5°, respectively. The 2θ of the α-Fe(N) films shifts to a lower position, which is indicative of lattice expansion according to the Bragg equation of diffraction \( d = (\lambda/2)(1/\sin \theta) \), by incorporation of nitrogen into the α-Fe lattice. The film deposited at a bias voltage of −50 V has the highest intensity for all peaks, indicating the best crystallinity among all the investigated samples. The relative peak intensities of (200) and (112) \( (I_{200}/I_{110} \text{ and } I_{112}/I_{110}) \) are 46% and 54% for a randomly oriented iron according to the JCPDS-International diffraction database. However, the

![Figure 5.14 Bias dependence of the XRD profiles shows that the film deposited at −50 V bias voltage exhibits the highest intensity, indicating the best crystallinity among the samples.](image)
values of the $\alpha$-Fe(N) films in this study are much smaller: $I_{200} / I_{110} \leq 18\%$ and $I_{112} / I_{110} \leq 12\%$, indicating that the films possess a preferred orientation in the (110) plane. This is consistent with the findings of Takahashi et al\textsuperscript{206} and Oda et al\textsuperscript{207}, who also found the preferred (110) orientation in the Fe-N films deposited using the sputtering technique.

### 5.4.3 Magnetic properties

Figure 5.15 (a) shows the in-plane M-H loops of the films deposited using bias voltages of $-50$, $-100$, and $-400$ V. The loops exhibit a soft behavior with good squareness. The bias-voltage dependence of $4\pi M_S$ is shown in Figure 5.15 (b). The film deposited at the bias voltage of $-50$ V exhibits the largest value of $4\pi M_S$ (18 kG). With a further increase of the bias voltage, the $4\pi M_S$ decreases. The $M_S$ changes according to the surface morphology and the microstructure. The highest $4\pi M_S$ of film being deposited at a bias voltage of $-50$ V is due to the relatively high crystallinity and low surface roughness of the film, which are consistent with those reported by Iwatsubo et al\textsuperscript{208}.

### 5.4.4 Discussion

The mean ion charge state, $q$, for Fe is 1.82 and the intrinsic energy of Fe ions emitted from a cathode source $E_0$ is about 68 eV\textsuperscript{209}. As the deposition pressure is relatively low ($5 \times 10^{-5}$ torr), the energy loss resulting from collisions between Fe ions and nitrogen gas molecules is negligible. Thus, the energy of Fe ions that reaches the substrate surface can be estimated as: $E_{Fe} = E_0 - qV_b$, where $V_b$ represents the applied substrate bias voltage. The energy of the ions
that reach the substrate surface strongly affects the films quality. The energy of the ions can be

Figure 5.15 (a) The magnetic hysteresis loops of films deposited at bias voltage of −50, −100, and −400 V respectively. (b) Bias voltage effect on the $4\pi M_S$ of the films.
CHAPTER 5 Nitrogen-catalytic Effect

divided into three regions, which results in different surface morphologies and microstructures:

(1) When the bias voltage is zero, the energy of ions is low; the film grows with the ions accumulating on the surface. The resputtering effect is weak and the mobility of surface atoms is relatively low. The films hence have a rough surface and low crystallinity.

(2) When the bias voltage is −50 V, the energy of ions increases to an optimized level, the energetic ions then penetrate into the film subsurface and increase the mobility of the surface atoms. The vacancies near the surface that are produced by the bombarding ions are partially refilled by the newly arriving ions, which results in downward packing of material such that films grown in a densely packed structure have a smooth morphology, as was observed. However, the optimized bias voltage may vary from material to material. For example, instead of −50 V, as was observed in this study for Fe-N films, one study of the bias dependence of the surface of TiN films found that film deposited at a bias voltage of −100 V had the lowest surface roughness.

(3) When the bias voltage is higher than −50 V, the energy of ions is too high and the bombardment and resputtering effect on the film surface become intense. The high-energy ions penetrate deeply into the films. The fast-dropping deposition rates that occur when the bias voltage increases to −100 and −400 V are evidence of the
intense resputtering effect. Ions with higher energy transfer more momentum energy to the film surface and increase the mobility of surface atoms, which leads to an increase of the surface roughness, as was observed. The intense bombardment and the deeply penetrated ions also damage the formed crystal, leading to a poor crystallinity.
CHAPTER 6  RESULTS AND DISCUSSION III:

JOINT EFFECT OF PHYSICAL SIZE AND

NITRODATION ON $M_S$

From the discussion in CHAPTER 4, we learnt that at ambient temperature, the $M_S$ of a ferromagnetic nanosolid decreases with size, while the discussion in CHAPTER 5 indicated that nitridation could enhance the $M_S$ of iron. This raises the question of whether the $M_S$ enhancement of the nitridation could overcome the size-induced reduction of $M_S$. In this chapter, the joint effects of physical size and nitrogen catalysis on the thin Fe-N films are described. Three series of films were deposited, which were labeled Fe, Fe-(N-Poor), and Fe-(N-Rich) according to the nitrogen concentration. The detailed deposition conditions are shown in section 3.3.3.

6.1 Nitrogen-poor Fe-N films

The nitrogen concentration of the films calculated based on the XPS is about 8~10 at%. Figure 6.1 shows the XRD profiles of the samples. The profiles show three peaks at about 44.3°, 64.6°, and 82.2°, corresponding to (110), (200), and (112) planes of α-Fe(N), respectively. Figure 6.2 shows the substrate temperature’s, $T_S$, effect on grain size, which increases with the $T_S$. At substrate temperatures of 110, 170, 230, 290, and 350°C, the nanocrystalline grain sizes are about 4.5, 8.0, 8.3, 9.3, and 10.2 nm, respectively. This is easy to understand because a higher substrate temperature brings more energy to the deposited atoms, which benefits the grain growth.
CHAPTER 6 Joint effects on $M_S$

Figure 6.1 XRD profiles of Fe-(N-Poor) films with poor nitrogen concentration deposited at various substrate temperatures.

Figure 6.2 Substrate temperature $T_S$ dependence of grain size of the Fe-(N-Poor) films.
Figure 6.3 shows the in-plane hysteresis loops of Fe-(N-Poor) films. The $M_S$ decreases with the size, which is similar to those of Ni films, as discussed in section 4.3.

### 6.2 Nitrogen-rich Fe-N films

Nitrogen-rich Fe-N films have a nitrogen concentration of ~30 at%. The XRD profiles in Figure 6.4 exhibit typical $\zeta$-Fe$_2$N peaks such as (101), (002), and (100) at $2\theta$ of 43.0, 40.9, and 37.0, respectively. The peaks become sharp and intense as the $T_S$ increase. The calculated grain size shown in Figure 6.5 increases monotonically with $T_S$, being similar to that of the Fe-(N-Poor) films.

The grain size dependence of in-plane magnetization of Fe-(N-Rich) films at room temperature exhibits the same tendency of that in Fe-(N-Poor) films, as shown in Figure 6.6.

![Graph showing M-H loops of low-nitrogen content films.](image)

Figure 6.3 The M-H loops of low-nitrogen content films.
CHAPTER 6 Joint effects on $M_S$

Figure 6.4 XRD profiles of Fe-N films at various substrate temperatures.

Figure 6.5 $T_S$ dependence of the grain size of Fe-(N-Rich) films.
CHAPTER 6 Joint effects on $M_S$

Figure 6.6 The M-H loops of Fe-(N-Rich) films of various grain sizes.

Figure 6.7 compares the size dependence of $M_S$ for the nitrogen-poor and nitrogen-rich Fe-N films together with the pure iron thin films. The $4\pi M_S$ of all the films decrease with the grain size, which is consistent with the observations concerning Ni films as described in section 4.3. The BOLS theoretical predictions with $\alpha = 1.2$, 1.0, and 1.0 based on Eq (4.18) for Fe-(N-Poor), pure Fe, and Fe-(N-Rich) are also shown in Figure 6.7. During the theoretical calculation, the average bond lengths, $d$, for Fe-(N-Poor), pure Fe, and Fe-(N-Rich) were 0.251, 0.255, and 0.225 nm, respectively. The bulk $4\pi M_S(\infty)$ were 30.0, 22.2, and 8.0 kG, respectively.\textsuperscript{103} The decrease in Ms for the Fe-(N-Rich) films with grain size of 8.0 and 6.0 nm is far from the predictions, which may be due to the sensitive of the VSM machine and the low crystallinity of the films.
CHAPTER 6 Joint effects on $M_S$

It can be seen that, with the same grain size, the $4\pi M_S$ of Fe-(N-Poor) films is always higher than that of the Fe films, while the $4\pi M_S$ of Fe-(N-Rich) films is always lower than that of the Fe films, indicating that poor nitrogen concentration introduced into the iron films enhances the magnetization, while an excess of nitrogen decreases it. When the grain size of Fe-(N-Poor) films is larger than 8.0 nm, the $M_S$ is even higher than that of the bulk value of Fe ($4\pi M_S = 22.2$ kG). This indicates that the enhancement of the $M_S$ by nitridation can overcome the size-induced decrease of $M_S$ at ambient. On the other hand, the $4\pi M_S$ of Fe-(N-Poor) films with a grain size below 8 nm is lower than that of the value of bulk iron; however, it is still higher than that of the Fe films with the same grain sizes, which indicates that when we investigate the nitrogen catalytic effect on the $M_S$ of iron films, the size effect should be taken into consideration together with the nitridation effect.

![Figure 6.7 Physical size and nitrogen catalytic effect on the magnetization of iron thin films.](image)

Figure 6.7 Physical size and nitrogen catalytic effect on the magnetization of iron thin films.
CHAPTER 7 Application of BOLS: \( T_C \) suppression of ferroelectric and superconducting nanosolids

This section shows that the model of \( T_C \) suppression for ferromagnetic nanosolids can be extended to the \( T_C \) suppression of ferroelectric and superconducting nanosolids, which have been widely observed.\(^{211,212,213,214,215}\)

For the \( T_C \) suppression of ferroelectric systems, such as \( \text{PbTiO}_3 \), \( \text{BaTiO}_3 \), \( \text{PbZrO}_3 \), and \( \text{BaTiO}_3 \), three different approaches\(^{216}\) have been developed to investigate the occurrence of surface modes. They are: (1) a microscopic pseudospin theory based on the Ising model in a transverse field; (2) a classical and macroscopic Landau theory in which surface effects can be introduced phenomenologically; and (3) a polariton model appropriate for the very-long-wavelength region. Taking the surface and nonequilibrium energy into consideration, Zhong et al\(^{217}\) extended the Landau-type phenomenologically classical theory by introducing a surface extrapolation length, \( \delta \), to the size-dependent \( T_C \) suppression of ferroelectric nanosolids. However, the model fails to explain the thermal properties of \( \text{PbTiO}_3 \) and \( \text{PbZrO}_3 \) nanosolids. Following this, Bursill et al\(^{218}\) assumed that the phenomenological Landou-Ginzburg-Devonshire coefficients in the Gibbs energy would change with the particle size, thus solving this problem. An empirical equation widely used to fit the \( T_C \) suppression of ferroelectric nanosolids is given as:\(^{211,213}\)

\[
\Delta T_C / T_C(\infty) = C / (K_j - K_C)
\]

where \( C \) and the critical size, \( K_C \), are adjustable parameters. Note that if \( K_j = K_C \), Eq (7.1) corresponds to a singularity. (The correct form should be \( K_j + K_C \))
instead of $K_j - K_C$ in Eq (7.1).) Zhong et al\textsuperscript{219} considered the Ising model for the long-range interaction in dealing with the ferroelectric nanosolids by adjusting the $\sigma$ in the exchange strength $J_{ij} = J/r_{ij}^{\sigma}$. $\sigma = 0$ corresponds to an infinite-range interaction and $\sigma = \infty$ corresponds to a nearest-neighbor interaction. More recently, Jiang et al\textsuperscript{220} adapted their model for melting point suppression to the $T_C$ suppression of the ferroelectric nanosolids, which is expressed as:

$$\frac{\Delta T_C (K_j)}{T_C (\infty)} = \exp\left(-\frac{2S_0}{R_s \frac{K_j}{K_C} - 1}\right) - 1$$

(7.2)

where $S_0$ is the transition entropy and $R_s$ is the idea gas constant. Numerical match for the $T_C$ suppression of BaTiO\textsubscript{3} and PbTiO\textsubscript{3} nanosolids has been reached with the documented $S_0$ values. It was found by Jiang et al\textsuperscript{220} that the larger $K_C$ value corresponds to a smaller value of $S_0$.

The Curie temperature of a superconductive nanosolid is also suppressed by minimizing the particle size. The relation between the $T_C$ and the energy-level spacing for spherical dots was suggested as follows:\textsuperscript{221}

$$\ln\left(\frac{T_C (K_j)}{T_C (\infty)}\right) = \sum \left(\frac{2}{2M + 1}\right) \left\{ \tanh\left(\frac{\pi^2 (2M + 1) k_B T_C}{\delta}\right) - 1 \right\}$$

(7.3)

where $\delta$ is the energy sublevel splitting in the conduction or valence band that can be estimated with the Kubo formula:\textsuperscript{153} $\delta = 4E_F/3n \propto 1/V \propto K_j^{-3}$, where $E_F$ is the fermi energy of the bulk materials and $n$ is the number of valence/conduction electrons in the nanosolid. Index $M$ is the magnetic quantum number. However, the $T_C$ suppression of Pb embedded in the Al-Cu-V
matrix measured by Tsai et al\textsuperscript{215} could not fit this prediction. Instead, the trend of Pb $T_C$ suppression follows $A \exp(-B/K_j)$, with adjustable constants $A$ and $B$.

Briefly, the SSCL theory,\textsuperscript{29} as introduced in section 2.1.2, considers the correlation length, and the CN-imperfection model\textsuperscript{30} considers the loss of exchange bonds of atoms in the ferromagnetic surface region. A model for the $T_C$ suppression of superconductive MgB$_2$ nanosolids\textsuperscript{222,223,224} has yet to be developed. Nevertheless, all the models developed so far have contributed to the understanding of $T_C$ suppression from various perspectives. Consistent insight and a unification of the $T_C$ suppression of ferromagnetic, ferroelectric, and superconductive nanosolids are highly desirable. Here, we show that an extension of the BOLS correlation to high-order atomic CN in conjunction with the Ising model could solve this problem.

The same shell structure to that expressed in Eq (4.15) can be used. However, for the dipole-dipole exchange interaction in a ferroelectric material, we need to consider high-order CN imperfection. For a ferroelectric spherical dot with radius $R = K_jl$, we need to consider the interaction between the specific central atom and its surrounding neighbors within the critical volume $V_C = 4\pi K_c^3/3$, in addition to the BOLS correlation in the surface region. The ferroelectric property drops down from the bulk value to a value smaller than $5/16$ (estimated from Figure 7.1 (b)) when one goes from the central atom to the edge along the radius. If the surrounding volume of the central atom is smaller than the critical $V_C$, the ferroelectrics of this central atom attenuate; otherwise, a bulk value remains. For an atom in the $i$th surface layer, the number of lost exchange bonds is proportional to the volume $V_{vac}$; that is, the volume
difference between the two caps of the $V_C$-sized spheres as illustrated in Figure 7.1 (b). Therefore, the relative change of the ferroelectric exchange energy of an atom in the $i$th atomic layer compared to that of a bulk atom becomes:

$$\frac{\Delta E_{\text{exc},i}}{E_{\text{exc}}(\infty)} = \frac{V_C - V_{\text{vac}}}{V_C} - 1 = -\frac{V_{\text{vac}}}{V_C} \quad (7.4)$$

Substituting Eq. (7.4) for the $z_{ib,c}^{-m}$ in Eq. (4.16) and considering the BOLS correlation in the surface region, we have a universal form for ferromagnetic, ferroelectric, and superconductive nanosolids ($m = 1$ in the Ising model):

$$\frac{\Delta T_C(R)}{T_C(\infty)} = \frac{\Delta E_{\text{exc}}(R)}{E_{\text{exc}}(\infty)} = \begin{cases} \sum_{i \leq 3} \gamma_i (z_{ib,c}^{-1} - 1) = \Delta_{\text{coh}} & \text{(Ferromagnetic)} \\ \sum_{i \leq K_c} \gamma_i \left(-\frac{V_{\text{vac}}}{V_C}\right) + \Delta_{\text{coh}} = \Delta_{\text{COH}} & \text{(else)} \end{cases} \quad (7.5)$$

$V_{\text{vac}}$ is the volume difference between the two spherical caps as illustrated in Figure 7.1. For the short spin-spin interaction, it is sufficient to sum over the

![Figure 7.1](image_url)

Figure 7.1 Schematic illustration of (a) short-range exchange loss for ferromagnetic nanoparticle, where only the nearest neighbor is considered; and (b) high-order exchange bonds loss of an atom in a spherical nanosolid with radius $R = K_d$. $K_c$ is the critical radius; the lost $V_{\text{vac}}$ (the shaded portion) is calculated by differencing the volumes of the two spherical caps:

$$V_{\text{vac}} = \pi(K_c + K_j - K_j \cos \theta)^2 \left(K_c + K_j - K_j \cos \theta - \frac{\pi}{3}(K_j - K_j \cos \theta)\right)^2 \left(K_j - K_j \cos \theta - \frac{\pi}{3}(K_j - K_j \cos \theta)\right),$$

where the angle $\theta$ is determined by the triangle $O_1O_2A$. 90°
Figure 7.2. $T_c$ suppression of (a) PbTiO$_3$,\textsuperscript{212} SrBi$_2$Ta$_2$O$_9$,\textsuperscript{213} BaTiO$_3$,\textsuperscript{225} and PbZrO$_3$\textsuperscript{226} nanosolids; and (b) superconductive MgB$_2$-1,\textsuperscript{214} MgB$_2$-2,\textsuperscript{227} and Pb\textsuperscript{215} nanosolids. $K_C$ is the critical correlation radius.\textsuperscript{90}
outermost three atomic layers, whereas for a ferroelectric or a superconductive solid, the sum should be within the sphere of radius $K_C$. A C-language source code for the calculation of the loss of long-range exchange energy as in Eq (7.5) is attached in Appendix II.

Least-squares linearization of the measured size-dependent $T_C$ represented by Eq. (7.1) gives the slope $B'$ and an intercept that corresponds to the bulk $T_C(\infty)$. The measured data may need calibration by matching the intercept to the $T_C(\infty)$. Compared with Eq (7.5), one would find that $B' = R\Delta_{\text{coh}}$ for a ferroelectric system and then the adjustable $K_C$ is obtained by computing optimization. For a ferromagnetic system, $B' = R\Delta_{\text{coh}}$, without needing numerical optimization. For a ferroelectric system, we need to optimize the $K_C$ value in the computation to match the theoretical curve to the measured data. Figure 7.2 (a) shows the $T_C$ suppression of ferroelectric PbTiO$_3$, SrBi$_2$Ta$_2$O$_9$, BaTiO$_3$, and antiferroelectric PbZrO$_3$ nanosolids. Calculations of optimized $K_C$ values for PbTiO$_3$, PbZrO$_3$, BaTiO$_3$, and SrBi$_2$Ta$_2$O$_9$ are listed in Table 7.1. For ferroelectric and superconductive nanosolids, $T_C = 0$ happens at $V_{\text{vac}} = V_C$, which means that the $K_j = K_C$ corresponds not to $T_C = 0$, but to a value that is too low to be detected. Figure 7.3 shows the $K_C$ dependence of the $T_C$ shift. For example, when $K_C = 5$, the bond contraction lowers the $T_C$ by -41.1%, the volume loss contribution lowers the $T_C$ by -53%, and the overall $T_C$ shift is -94%. The difference in the optimized $K_C$ using different approaches, as compared in Table 7.1, lies in that the slope ($S/V$ ratio) in the current approach is not a constant but changes with the particle size.
CHAPTER 7 Application of BOLS

Figure 7.3 Critical correlation radius $K_C$ dependence of the $T_C$ shift of ferroelectric and superconductive alloying nanosolids. For the $K_C = 5$ example, the bond contraction lowers the $T_C$ by -41.1% and the high-order bond lost (Bond lost) contribution that is a constant lowers the $T_C$ by -53%, and the overall $T_C$ shift is -94%. $K_C \leq 4$, $T_C = 0.90$

Applying the BOLS prediction to the scattered $T_C$ suppression of superconductive MgB$_2$ nanosolids (Figure 7.2 (b)) leads to an estimation of the critical radius, $K_C = 3.5$, which agrees with that determined recently by Li et al ($R_C \sim 1.25$ nm).\textsuperscript{227} The consistency of the BOLS prediction with the experiment data indicates that the long-range interaction dominates the superconductive $T_C$.

For Al-Cu-V-embedded Pb nanosolid,\textsuperscript{215} the $K_C$ is around 1, which is the same as that for a ferromagnetic solid. This finding provides a mechanism for the origin of the superconductive $T_C$ suppression of MgB$_2$ nanosolids.
Table 7.1 Summary of information on the bulk atomic diameter, $d$, $T_C(\infty)$, and the critical radius $K_C$ at which the central atom lost its ferroelectricity attenuates. $K_C \leq 4$ corresponds to $T_C = 0$. The critical radius $R'_C$ at which $T_C = 0$ is derived by other models. 

<table>
<thead>
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<th>Materials</th>
<th>$d$/nm</th>
<th>$T_C(\infty)/K$</th>
<th>$K_C/R_C$/nm</th>
<th>$R'_C$/nm (Ref)</th>
</tr>
</thead>
<tbody>
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<td>Fe</td>
<td>0.252</td>
<td>1043</td>
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<td>0\textsuperscript{10}</td>
</tr>
<tr>
<td>Co</td>
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<td>0\textsuperscript{12}</td>
</tr>
<tr>
<td>Ni</td>
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<td>1</td>
<td>0\textsuperscript{85}</td>
</tr>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4}</td>
<td>0.222</td>
<td>860</td>
<td>1</td>
<td>0\textsuperscript{79}</td>
</tr>
<tr>
<td>PbTiO\textsubscript{3}</td>
<td>0.283</td>
<td>773</td>
<td>4/1.04</td>
<td>6.3\textsuperscript{211}, 4.5\textsuperscript{212}</td>
</tr>
<tr>
<td>SrBi\textsubscript{2}Ta\textsubscript{2}O\textsubscript{9}</td>
<td>0.270</td>
<td>605</td>
<td>4/1.0</td>
<td>1.3\textsuperscript{213}</td>
</tr>
<tr>
<td>PbZrO\textsubscript{3}</td>
<td>0.288</td>
<td>513</td>
<td>8/2.3</td>
<td>15\textsuperscript{226}</td>
</tr>
<tr>
<td>BaTiO\textsubscript{3}</td>
<td>0.243</td>
<td>403</td>
<td>100/24.3</td>
<td>24.5\textsuperscript{228}, 55\textsuperscript{225}</td>
</tr>
<tr>
<td>MgB\textsubscript{2}</td>
<td>0.352</td>
<td>41.7</td>
<td>3.5/1.25</td>
<td>1.25\textsuperscript{227}</td>
</tr>
<tr>
<td>Pb</td>
<td>0.349</td>
<td>7.2</td>
<td>3.5/1.25</td>
<td>1.25\textsuperscript{215}</td>
</tr>
</tbody>
</table>
CHAPTER 8 CONCLUSIONS and RECOMMENDATIONS

8.1 Conclusions

The physical size effect, the nitrogen catalytic effect, and their joint effect on the magnetic properties of iron nanosolids were studied using theoretical, simulative, and experimental approaches, which are summarized as follows:

- Theoretically, in the first-order approximation, using the concept of “molecular field,” and incorporating the BOLS correlation mechanism into the Brillouin function, a model was developed to explain the $T_C$ suppression and the size-induced $M_S$ shift at various temperatures. Theoretical predictions for the size-induced $H_C$ and nitridation effect on the $M_S$ of iron films were also presented.

- Simulatively, the BOLS correlation premise was incorporated into the Ising model. Monte Carlo simulation was then carried out on the spin system with various cluster sizes and geometric shapes to verify the size-induced $M_S$ shift and $T_C$ shift.

- Experimentally, Ni, Fe, and Fe-N films were deposited using the FCVA technique, the size-induced $H_C$ and $M_S$ for nickel films at ambient temperature were examined as well as the nitridation effect on the $M_S$ of iron films and the joint effect of physical size and nitridation on the $M_S$ of Fe-N films.

The major findings include:
CHAPTER 8 Conclusion and Recommendations

- Miniaturization of the ferromagnetic solid size lowers the $T_C$ of a ferromagnetic nanosolid, in general, due to the tailoring of cohesive energy/exchange energy, which contributes to the spin order. This idea can also be applied to the $T_C$ suppression of ferroelectric and superconducting nanosolids by extending the BOLS correlation to high-order CN imperfection.

- Incorporating the BOLS correlation premise into the Brillouin equation gives an expression for the size dependence of $M_S$ at various temperatures. It is clarified for the first time that: (i) At very low temperatures, the $M_S$ increases inversely with size due to the localization of the charges that contribute to the angular momentum, $J$, and hence the magnetic moment, $\mu$, at the surface sites or at the sites surrounding defects. (ii) At temperatures in the vicinity of the $T_C$, the $M_S$ decreases with the particle size due to the decrease in cohesive energy/exchange energy, which results in a lower level of spin order.

- The $H_C$ of a freestanding ferromagnetic nanosolid may possess a superparamagnetic state. However, for nanocrystalline thin films, the intergrain exchange energy increases with the decrease in grain size, resulting in an increased $H_C$.

- When low nitrogen concentration is introduced into the iron films, the $M_S$ is enhanced. It is even higher than that of the bulk pure iron when the nitrogen concentration is around 10%. However, excess nitrogen concentration decreases the $M_S$. The enhancement of the $M_S$ originates from the formation of high magnetic moment iron valence states such as $\text{Fe}^+$ or even $\text{Fe}^{\text{dipole}}$ when nitrogen is limited. If excess nitrogen is
introduced, the vanishing of $F_{\text{dipole}}$ decreases the magnetization due to the electron’s being captured by the nitrogen atom.

- **Size-induced** $M_S$ reduction at ambient temperature may affect the applications of nanosolids; thin Fe-N films have the joint effect of the physical size and nitrogen catalysis. When the grain size is larger than ~8 nm, with low nitrogen concentration (~10 at%), the enhancement of nitridation overcomes the suppression of the physical size effect, leading to an $M_S$ larger than that of the bulk Fe.

- Additionally, the FCVA technique has been proven to be a compatible technique for magnetic thin film deposition. It is versatile, flexible, and cost effective. By optimizing the parameters, such as bias voltages, substrate temperature, and working pressure, magnetic thin films with a smooth surface, a dense and nanocrystalline structure, and good magnetic properties can be obtained. In particular, the bias voltages that control the ions’ energy affect the films’ properties. ~50 V is demonstrated to be an optimized deposition bias voltage for magnetic Fe-N films to obtain the smoothest surface, highest crystallinity, and, accordingly, the highest $M_S$.

The consistency between the theory predictions, Monte Carlo simulation, and the experimental observations not only reconciles the discrepancy of the observations but also deepens our insight into the physical origins of the size-induced $M_S$ shift, $T_C$ suppression, $H_C$ shift, and the nitridation effect on $M_S$. The $M_S$ and $T_C$ relate to spin-spin exchange energy/cohesive energy, while the $H_C$ relates to the intergrain exchange energy. The $M_S$ also relates to the $\mu$ of
individual atoms that is affected both by the charge localization due to bond contraction and by nitrogen addition, which alters the valence value of the Fe atoms. The study may prompt a more feasible mechanism for adjusting the magnetic behavior of the films by means of both physical shape and size and chemical reaction. Successful deposition of Fe-N films using FCVA technology amplifies the capacity of the FCVA technique in the reactive deposition of magnetic materials.

8.2 Recommendations for further research

Further study of the size effect of freestanding particles at various temperatures, especially very low temperatures, with precise controlling of the temperature will add to the understanding of nanomagnetism. Also, further study of magnetic nanostructural devices such as the giant magneto resistance with multilayers of Fe-N/Cr using Fe-N thin films may lead to new applications of Fe-N thin films.

The Ni and Fe-N films produced by the FCVA technique possess good magnetic properties with a smooth surface and a small crystalline size. The thin films of magnetic Ni, Fe, and Fe-N are very suitable for the seed layer of carbon nanotubes, which educes further study of the growth of carbon nanotubes and the corresponding applications based on them.
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130

Bibliography


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Appendix I Monte Carlo simulation

Appendix I

C language program of Monte Carlo simulation

/*
ising.c
Monte Carlo simulation of the 3-D Ising model of magnetic materials
*/

#include <stdio.h>
#include <stdlib.h>
#include <math.h>
#include <string.h>
#include <ctype.h>
#include "RanGen.h"

#define  L_MAX  80
int D;   /*Number of spins in one direction, diameter of the particle */
int N = 0;     /* total number of spins */
int layernumber=20; /* global variable, layer number is determined by the shell number */

int spin[L_MAX][L_MAX][L_MAX];       /* spin values */
/* The value is 0,-1,or 1. 0 indicates that there is no atom in the sites, -1 means the spin down, and 1 means spin up */

int S=6;      /*shell number of the system*/
int diametersquare[L_MAX*L_MAX];     /*The square of the radius of the system with every shell number */

double radia[L_MAX][L_MAX][L_MAX];  /*To store the radius of each atoms */

int center=0;     /* the center of the particle: (center,center,center)*/

int next[L_MAX], prev[L_MAX];
int Neighbors[13];

int MonteCarloSteps;    /* number of Monte Carlo steps per spin */

double J = 1.0;     /* coupling +1=ferro, -1=antiferro */
double T = 2.4;     /* temperature */
double w[49][3];     /* pre-computed Boltzmann factors */

int SS;      /* sum of s_i*s_j */
double E;   /* current energy */
double M;   /* current magnetization */
Appendix I Monte Carlo simulation

```c
int flips;                   /* spin flips in current sweep of lattice */

unsigned long randomSeed = 200;

int hotStart = 0;
double H = 1.2;              /* applied magnetic field */

int thermalizationSteps = 5000;
int productionSteps = 5000;
int stepsPerBlock = 500;
int blocks;

int measurements;
double E_sum, E_sqd_sum, M_sum, M_sqd_sum, abs_M_sum, acceptance_sum;
double E_block, E_block_sum, E_block_sqd_sum;

void calculateDofshell(void);
void printBoltzmannFactors(FILE *file);
void printDofshell(FILE *file);
void computeBoltzmannFactors(void);
void particleestablish (void);
void printparticle (FILE *file);
void initialize(FILE *file);
void measureProperties(void);
void oneMonteCarloStep(FILE *file);
void printHeader(FILE *file);
void printProperties(FILE *file);
void printBlockProperties(FILE *file);
void zeroProperties(void);

int main (int argc, char *argv[]) {
    int i, step, block,TT,HH;
    FILE *fp;

    for (i = 1; i < argc; i++) {
        if (strchr(argv[i], '='))
            switch (toupper(*argv[i])) {
                case 'S':
                    sscanf(argv[i] + 2, "%d", &S);
                    break;
                case 'T':
                    sscanf(argv[i] + 2, "%lf", &T);
                    break;
                default:
                    break;
            }
    }

    fp=fopen("Formal-TSH.txt","w"); /* file for output */
    calculateDofshell();
    printDofshell(fp);
    fprintf(fp,"Monte Carlo Simulation of the 3-D Ising Model\n");
    fprintf(fp,"=======================================\n");
    fprintf(fp,"Temperature| shell |   N  |   H       |         | (|M|/N)  |  (E/N)   |      Sus/N  |
     (C/N)   |accept ratio|\n");
```

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Appendix I Monte Carlo simulation

for (S=2; S<6; S++)
    {
        for (TT=0; TT<16; TT+=2)
            {
                for (HH=0; HH<=0; HH++)
                    {
                        H=HH/10.0;
                        if (TT==0)
                            T=TT+0.1;
                        else T=TT;
                        if (T<6)
                            hotStart=0;
                        else
                            hotStart=1;
                        layernumber=(int)(sqrt(diametersquare[S]))+1;
                        fprintf(fp,"  %6.2f   %5d    ",T,S);
                        /*output the temperature and the shell number of
                           the particle*/
                        N=0;
                        particleestablish();
                        initialize(fp);
                        printparticle(fp);
                        fprintf(fp,"%d ", N);
                        /*output the total spin number of the particle*/
                        fprintf(fp,"%f ", H);
                        /*output the applied magnetic field*/
                        printf("Performing %d thermalization steps ...", thermalizationSteps);
                        printBoltzmannFactors(fp);
                        for (step = 0; step < thermalizationSteps; step++)
                            oneMonteCarloStep(fp);
                        printf(" done thermalization steps\n");
                        zeroProperties();
                        printf("Performing %d production steps\n", productionSteps);
                        /*printHeader(fp);*/
                        for (step = 0; step < productionSteps; step++)
                            { }
                        oneMonteCarloStep(fp);
                        measureProperties();
                        if (MonteCarloSteps % 500 == 0)
                            printProperties(stdout);
                        }
                        printProperties(fp);
                        /*fprintf(fp,"\n");*/
                        zeroProperties;
                        printBlockProperties(stdout);
Appendix I Monte Carlo simulation

}/*end of for*/
} /*end of for*/
}/*end of for*/
fclose(fp);
return 0;
}

void computeBoltzmannFactors(void)
{
int i;
for (i = -24; i <= 24; i += 2)
{
    w[i + 24][0] = exp( - (i*J + 2 * H) / T);
    w[i + 24][2] = exp( - (i*J - 2 * H) / T);
}
}

void printBoltzmannFactors(FILE *file)
{
int i;
for (i = 0; i <= 48; i += 4)
    fprintf(file, "SumOfNeighbors: %d, BoltzmannFactors: %9.6f\n", (i-24)/2, w[i][0]);
for (i = 0; i <= 48; i += 4)
    fprintf(file, "Index: %d, SumOfNeighbors: %d, BoltzmannFactors: %9.6f\n", i, (i-24)/2, w[i][2]);
}

void particleestablish(void)
{
int i,j,k;
D = 2*layerNumber+3;
/* D should be always smaller than L_MAX */
for (i=0;i<L_MAX;i++)
    for (j=0;j<L_MAX;j++)
        for (k=0;k<L_MAX;k++)
            spin[i][j][k]=0;

for (i=0;i<=layerNumber;i++)
    for (j=0;j<=layerNumber;j++)
        for (k=0;k<=layerNumber;k++)
            {
            spin[i+i][j+j][k+k]=1;
            spin[2*i+1][2*j+1][2*k]=1;
            spin[2*i+1][2*j][2*k+1]=1;
            spin[2*i][2*j+1][2*k+1]=1;
            }
Appendix I Monte Carlo simulation

```c
if (spin[layernumber][layernumber][layernumber] = = 0)
    center=layernumber+1;
else
    center=layernumber;

for (i=0;i<=D+2;i++)
    for (j=0;j<=D+2;j++)
        for (k=0;k<=D+2;k++)
            if (spin[i][j][k] != 0)
                if (((i-center)*(i-center)+(j-center)*(j-center)
                    +(k-center)*(k-center))>diametersquare[S])
                    spin[i][j][k]=0;
            else
                N++;

void initialize ( FILE *file)
{
    int i, x, y, z;

    qad_init(1,randomSeed);

    if (hotStart)
        {
            for (x = 0; x <= D; x++)
                for (y = 0; y <= D; y++)
                    for (z = 0; z <= D; z++)
                        {
                            if (spin[x][y][z] != 0)
                                /*fprintf (file,"flag1");*/
                                if (qad_rand(0)<0.5)
                                    { spin[x][y][z] = 1;
                                    /*fprintf(file,"%10.5f\n", qad_rand(0));*/
                                    } else spin[x][y][z] = -1;
                        }
    }
    else
        {
            for (x = 0; x <= D; x++)
                for (y = 0; y <= D; y++)
                    for (z = 0; z <= D; z++)
                        if (spin[x][y][z] != 0)
                            if (J < 0 && (x + y + z) % 3)
                                spin[x][y][z] = -1;
                            else
                                spin[x][y][z] = 1;
        }

    /* arrays for periodic boundary conditions */
    for (i = 0; i <= D; i++)
        { /*
```
```
Appendix I Monte Carlo simulation

```c
next[i] = i + 1;
prev[i] = i - 1;
}

/*
next[D - 1] = 0;
prev[0] = D - 1;
*/

/* compute spin sums */
M = SS = 0;
for (x = 0; x <= D; x++)
    for (y = 0; y <= D; y++)
        for (z = 0; z <= D; z++)
            {  
                if (spin[x][y][z] != 0)
                      { 
                          M += spin[x][y][z];
                          Neighbors[1]=spin[2*center-x][2*center-y][z];
                          Neighbors[2]=spin[x][2*center-y][2*center-z];
                          Neighbors[3]=spin[2*center-x][y][2*center-z];
                          Neighbors[4]=spin[x][y][2*center-z];
                          Neighbors[5]=spin[2*center-x][y][z];
                          Neighbors[6]=spin[x][2*center-y][z];
                          SS +=
                      }
            }

E = - J * SS - H * M;
computeBoltzmannFactors();
MonteCarloSteps = 0;
}
void oneMonteCarloStep (FILE *file)
{
    int x, y,z, sum_of_neighbors, delta_SS;
    double ratio_of_Boltzmann_factors,temp;
    flips = 0;
    delta_SS=0;
    /* sweep the lattice */
    for (x = 0; x <= D; x++)
        {  
            for (y = 0; y <= D; y++)
                {  
                    for (z=0; z <= D; z++)
                        {  
                            if (spin[x][y][z]!=0)
                                {  
                                    Neighbors[1]=spin[2*center-x][2*center-y][z];
                                    
                                }
                        }
                    }
                }
```
Appendix I Monte Carlo simulation

Neighbors[2]=spin[x][2*center-y][2*center-z];
Neighbors[3]=spin[2*center-x][y][2*center-z];
Neighbors[4]=spin[x][y][2*center-z];
Neighbors[5]=spin[2*center-x][y][z];
Neighbors[6]=spin[x][2*center-y][z];
Neighbors[7]=spin[x][y][2*center-z];
Neighbors[8]=spin[2*center-x][y][z];
Neighbors[9]=spin[x][2*center-y][z];
Neighbors[10]=spin[x][2*center-y][2*center-z];
Neighbors[12]=spin[2*center-x][2*center-y][z];

sum_of_neighbors=

delta_SS = 2*spin[x][y][z] * sum_of_neighbors;
ratio_of_Boltzmann_factors = w[delta_SS + 24][spin[x][y][z] + 1];

if ((temp=qad_rand(0)) < ratio_of_Boltzmann_factors)
{
    spin[x][y][z] = -spin[x][y][z];
    M +=2*spin[x][y][z];
    SS -= delta_SS;
    ++flips;
}

E = - J * SS - H * M;
++MonteCarloSteps;

void zeroProperties (void)
{
    E_sum = E_sqd_sum = M_sum = M_sqd_sum = abs_M_sum = 0;
    E_block = E_block_sum = E_block_sqd_sum = 0;
    acceptance_sum = 0;
    measurements = 0;
    blocks = 0;
}

void measureProperties (void)
{
    M_sum += M;
    M_sqd_sum += M * M;
}
Appendix I Monte Carlo simulation

```c
abs_M_sum += fabs(M);
E_sum += E;
E_sqd_sum += E * E;
acceptance_sum += flips;
++measurements;

if (MonteCarloSteps % stepsPerBlock == 0) {
    double avg = E_block / stepsPerBlock;
    E_block_sum += avg;
    E_block_sqd_sum += avg * avg;
    ++blocks;
    E_block = 0;
} else {
    E_block += E;
}
}

void printHeader (FILE *file) {
    int i;
    fprintf(file, "   MC Step ");
    fprintf(file, "   \|M\|/N  ");
    fprintf(file, "     E /N   ");
    fprintf(file, "    Sus/N   ");
    fprintf(file, "    C /N    ");
    fprintf(file, "   accept ratio
");
    for (i = 0; i < 6; i++)
        fprintf(file, "-----------
");
}

void printProperties (FILE *file) {
    double norm, avg;
    /* measurement number */
    fprintf(file, "  % 8d  ", measurements);
    norm = N;
    if (measurements > 0)
        norm *= measurements;
    /* average magnetization per spin */
    fprintf(file, "% 9.6f  ", abs_M_sum / norm);
    /* average energy per spin */
    fprintf(file, "% 9.6f  ", E_sum / norm);
    /* average susceptibility per spin */
    avg = M_sum / norm;
    avg = (M_sqd_sum / norm - N * avg * avg) / T;
    fprintf(file, "% 9.6f  ", avg);
    /* average heat capacity per spin */
    avg = E_sum / norm;
    avg = (E_sqd_sum / norm - N * avg * avg) / (T * T);
    fprintf(file, "% 9.6f  ", avg);
    /* average acceptance ratio */
    fprintf(file, "% 9.6f\n", acceptance_sum / norm);
    /*fprintf(file, "norm:%5d,N:%5d,M:%5d\n",norm,N,M);*/
    /*fprintf(file, "absM_sum: % 9d  norm: % 9d   N: % 9d\n", abs_M_sum, norm, N);*/
```

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Appendix I Monte Carlo simulation

void printBlockProperties (FILE *file)
{
    double avg, std_dev;

    avg = E_sum / measurements;
    std_dev = E_sqd_sum / measurements;
    std_dev = sqrt(std_dev - avg * avg);
    avg /= N;
    std_dev /= N;

    fprintf(file, "printblockproperties\n" );
    fprintf(file, " = %f +- %f
", avg, std_dev / sqrt(measurements));

    avg = E_block_sum / blocks;
    std_dev = E_block_sqd_sum / blocks;
    std_dev = sqrt(std_dev - avg * avg);
    avg /= N;
    std_dev /= N;

    fprintf(file, "Number of blocks = %d
", blocks);
    fprintf(file, " = %f +- %f
", avg, std_dev / sqrt(blocks));
}

void printparticle (FILE *file)
{
    int x,y,z;
    fprintf(file, "spin system of the particle:\n");
    for (x=0;x<=D;x++)
    {
        fprintf(file, "section \6d\n",x);
        for (y=0;y<=D;y++)
        {
            for (z=0;z<=D;z++)
                fprintf(file, \3d,spin[x][y][z]);

            fprintf(file,"\n");
        }
    }
}

void calculateDofshell (void)
{
    int i,j,k,LMAX,L_MAX,shellnumber;
    short int sp[L_MAX][L_MAX][L_MAX];

    for (i=0;i<L_MAX;i++)
        for (j=0;j<L_MAX;j++)
            for (k=0;k<L_MAX;k++)
                sp[i][j][k]=0;

    for (i=0;i<L_MAX/2-1;i++)
        for (j=0;j<L_MAX/2-1;j++)
            for (k=0;k<L_MAX/2-1;k++)
                sp[i][i][k+k]=1;
    sp[2*i+1][2*i+1][2*k]=-1;
    sp[2*i+1][2*j][2*k+1]=-1;
    sp[2*i][2*j+1][2*k+1]=-1;
}
Appendix I Monte Carlo simulation

LMAXLMAX=L_MAX*L_MAX;
shellnumber=1;

for (x=1;x<LMAXLMAX;x++)
{
    y=0;
    for (i=0;i<L_MAX-1&&y==0;i++)
        for (j=0;j<L_MAX-1&&y==0;j++)
            for (k=0;k<L_MAX-1&&y==0;k++)
                if (sp[i][j][k]!=0)
                    if (i*i+j*j+k*k==x)
                        y=1;

    if (y==1)
        shellnumber++;
diametersquare[shellnumber]=z;
}

/*there is an atom in the center in this situation */

void printDofshell (FILE *file)
{
    int i,LMAXLMAX;
    double d;
    LMAXLMAX=L_MAX*L_MAX;
    fprintf(file, "the shell diameter of each shell:");
    for (i=0;i<L_MAX;i++)
        d=sqrt(diametersquare[i]);
        fprintf(file, "%4d:%8.4f  ", i, d);
    if (i%5==0)
        fprintf(file,"\n");
}

/* RanGen.h
 * Quick And Dirty Random Number Generator
 * Based on the quick and dirty generator in "Numerical Recipes"
 * Parallelized using a simple leapfrog algorithm
 */

#ifndef _QADRNG_H_
define _QADRNG_H_ 1
#include <stdio.h>
#include <stdlib.h>
define QAD_MODULUS 4294967296.0
define QAD_MULTIPLIER 1664525L
define QAD_INCREMENT 1013904223L
define QAD_MAX_PROCS 256
static unsigned long qad_seed[QAD_MAX_PROCS];
Appendix I Monte Carlo simulation

static unsigned long qad_mult;
static unsigned long qad_incr;
static int qad_procs = 1;

static void qad_init (int processes, unsigned long seed)
{
    int i;

    if (processes < 1 || processes > QAD_MAX_PROCS)
    {
        fprintf(stderr, "qad_init: numprocs = %d \n", processes);
        fprintf(stderr, " must be in range [1, %d]\n", QAD_MAX_PROCS);
        exit(1);
    }
    else qad_procs = processes;

    for (i = 0; i < processes; i++)
    {
        qad_seed[i] = seed;
        seed = QAD_MULTIPLIER * seed + QAD_INCREMENT;
    }

    qad_mult = QAD_MULTIPLIER;
    qad_incr = QAD_INCREMENT;
    for (i = 1; i < processes; i++)
    {
        qad_mult *= QAD_MULTIPLIER;
        qad_incr = QAD_INCREMENT * (qad_mult - 1) / (QAD_MULTIPLIER - 1);
    }
}

static unsigned long qad_get_seed (void)
{
    return qad_seed[0];
}

static double qad_rand (int process)
{
    qad_seed[process] = qad_mult * qad_seed[process] + qad_incr;
    return qad_seed[process] / QAD_MODULUS;
}

#define QAD RAND(process) \n( (qad_seed[(process)] = \n    qad_mult * qad_seed[(process)] + qad_incr ) / QAD_MODULUS )

#ifndef QADRNG_H
# endif /* QADRNG_H */
Appendix II

C language program for the calculation of long-range exchange energy loss

```c
#include <stdio.h>
#include <stdlib.h>
#include <math.h>
#include <string.h>
#include <ctype.h>

int main ()
{
    int i, ShellNumber, RangeOfExchange, K;
    double DeltaShift, VOIFLost, Shift, SToVRatio;
    double s, sinr, cosr, h1, V1, V2,R,d,r;

    FILE *fp;
    fp=fopen("tempout.txt","w");

    //initialize:
    RangeOfExchange=100;

    for (ShellNumber=1; ShellNumber<=400; ShellNumber++)
    {
        //ShellNumber=50;
        Shift=0;
        for (i=1; i<=RangeOfExchange; i++)
        {
            if ((K=ShellNumber-i)<=0)
                break;
            else
            {
                //calculate one shell
                SToVRatio=3.0/ShellNumber*(1-(i-0.5)/ShellNumber )*(1-(i-0.5)/ShellNumber);

                //calculate the lost volume ratio of exchange
                R=ShellNumber;
                d=K;
                r=RangeOfExchange;
                s=(R+d+r)/2;
                sinr=sqrt(s*(s-R)*(s-d)*(s-r))/(R*d/2);
                cosr=sqrt(1-sinr*sinr);
                h1=R-R*cosr;
                V1=3.14*h1*h1*(R-h1/3);
                V2=3.14*(r+d-R*cosr)*(r+d-R*cosr)*(r-(r+d-R*cosr)/3);
                VOIFLost=(V2-V1)/(4*3.14*r*r*r/3);

                DeltaShift=SToVRatio*(-VOIFLost);
                Shift=Shift+DeltaShift;
            }
        }
        fprintf(fp, "  %d    %f
", ShellNumber,Shift*100);
    }
}
```
Appendix II Source code for the calculation of long-range exchange energy loss

}