MAGNETIZATION OF CU GeO$_3$
MAGNETIZATION OF CUGEO$_3$

By

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A Thesis

Submitted to the School of Graduate Studies

in Partial Fulfillment of the Requirements

for the Degree

Master of Science

McMaster University

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TITeL: Magnetization of CuGeO₃

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NUMBER OF PAGES: vii, 49
Abstract

As the first inorganic spin-Peierls compound, CuGeO$_3$ can be described with an AF Heisenberg model. The magnetization process of CuGeO$_3$ is studied using the numerical Density Matrix Renormalization Group (DMRG) technique. The $M-H$ curve of CuGeO$_3$ and other one dimensional Heisenberg systems are described, and their different nature are analyzed. In particular, the middle field cusp singularity appears in the $M-H$ curve of CuGeO$_3$ is described.
Acknowledgement

Firstly I would like to thank my supervisor, Dr. Erik Sorensen for all the help he gave me with my research work, especially for his patience, support, and guidance.

I would also like to thank Dr. John Berlinsky and Dr. Catherine Kallin for their valuable suggestions to my thesis.

I would also like to thank my classmates for their help to my study and their friendship.

And last, thanks go to my husband, Guodong, my daughter, Weiran, my mother and my sisters for their support during these two years.
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Chapter 1

Introduction

Since the discovery of CuGeO$_3$ as the first inorganic spin-Peierls (SP) compound [1], this substance has attracted much attention both theoretically and experimentally.

The spin-Peierls transition has been investigated for more than two decades for several model materials, but only for organic substances, which were difficult to grow in large single crystals and in which the doping or substitution of impurities was not easy. The discovery of CuGeO$_3$, as an inorganic spin-Peierls compound invigorated this study greatly. Large crystals of high quality can now be synthesized allowing for a variety of very precise experimental studies. The quasi 1-d chain structure which is embedded in a relatively simple 3-d lattice structure facilitates understanding of the experimental results. Furthermore, CuGeO$_3$ can be easily doped. This makes detailed investigations of the observed antiferromagnetism, which occurs under doping, possible.
The study of CuGeO$_3$ has attracted enormous theoretical and experimental efforts, particularly with regard to the magnetization of CuGeO$_3$, because the $M - H$ curve exhibits a variety of interesting behavior. The main purpose of this thesis is to describe the magnetization of CuGeO$_3$ and other 1-d AF Heisenberg systems, and to analyze their different nature.

Within the structure of CuGeO$_3$, there exists a 1-d antiferromagnetic (AF) interaction between spins on adjacent Cu$^{2+}$ ions in the $c$ direction. It can be modeled by a $S = 1/2$ zigzag spin ladder, and we can describe it with an AF Heisenberg model.

The basic method used in this thesis is the density matrix renormalization group (DMRG) approach. This numerical algorithm was developed by Steven White in 1992 [2, 3]. The DMRG technique is an extremely powerful tool for calculating properties of 1-d systems. Considering system sizes which can be handled, accuracy of the results and variety of models which can be treated, DMRG turns out to be superior to most other numerical approaches such as exact diagonalization or quantum Monte Carlo simulations.

An introduction to the DMRG algorithm is presented in the second chapter. In the third chapter, the structure of CuGeO$_3$ is described and the model
Hamiltonian is set up. In the fourth chapter, the magnetization of CuGeO$_3$ is described thoroughly. A summary and conclusion are given in chapter five.
Chapter 2

Density Matrix Renormalization Group

The density matrix renormalization group (DMRG) method, put forward by Steven White in 1992 [2, 3], has proven to be an extremely powerful technique for quasi 1-d quantum systems.

2.1 Renormalization Group Method

As we know, exact diagonalization studies are constrained due to the rapid increase in the dimension of the Hilbert space with increasing lattice size. On the other hand, in small lattice systems finite size effects must be considered in order to reduce the influence of their behavior. How does one deal with this dilemma? The renormalization group method provides a good solution to this question. The basic idea of all lattice renormalization group techniques is to enlarge the system iteratively but keeping only a constant number of basis states.

The standard numerical renormalization group method was first put forward
by Wilson to solve the Kondo problem [4]. In this procedure, one first breaks the infinite chain into identical blocks $B$ of $n$ sites and $m$ basis states each, and then diagonalizes the Hamiltonian matrix $H_{BB}$ for two neighboring blocks. Secondly, one uses the $m$ lowest-lying eigenstates to form the truncated basis for the new block $B'$, i.e. the superblock, which is twice as large as the old one, see Figure 2.1.

![Blocking scheme for standard numerical renormalization group.](image)

Figure 2.1: Blocking scheme for standard numerical renormalization group.

This procedure is done by

$$H_{B'} = OH_{BB}O^T,$$  \hspace{1cm} (2.1)

where $O$ is an $m \times m^2$ transformation matrix, formed by the eigenstates of $H_{BB}$.

This procedure is repeated using the new block $B'$ in the truncated
representation as the basis block. The basic assumption in this approach is that only the lowest-lying block eigenstates are relevant to the ground state of the final (infinite) system. However, this approach is flawed in its treatment of boundary conditions. The two neighboring blocks $B$ which are considered in one step are not connected to the rest of the chain. In particular, for free fermions the eigenstates of $B$ have nodes on the boundary whereas the superblock function $|\psi\rangle$ would have a nonzero amplitude at the boundary between the blocks. Therefore, the eigenstates which are kept as the new basis are likely to have inappropriate features at the edges for describing the block as part of an infinite chain (see Reference [3]). To remedy this flaw, White put forward the DMRG method [2, 3].

2.2 Density Matrix

The fundamental difficulty in the standard approach lies in the selection of the new basis states. How does one find an optimal truncated basis for a block $B$? White suggested that the optimal set of eigenstates to keep is determined by the reduced density matrix [2, 3]. Let us see how this works. For an isolated system at finite temperature, the probability that the block is in an eigenstate $i$ of the block Hamiltonian is proportional to its Boltzmann weight $e^{-\beta E_i}$, which
is also an eigenvalue of the density matrix. An eigenstate of the Hamiltonian is in this case also an eigenstate of the density matrix. Since the lowest energy corresponds to the largest Boltzmann weight, it is natural to keep the most probable eigenstates. On the other hand, if the system is interacting with its environment, e.g. a heat bath, its Hamiltonian and its density matrix no longer share the same set of eigenstates. Considering block $B$ as the system and the rest of the lattice to be a heat bath, then it is more reasonable to use the eigenstates of the density matrix rather than the eigenstates of the Hamiltonian to describe the system.

Let us look at the super-block configuration used by White [5] for the density matrix calculations, see Figure 2.2. We adopt the notation $B_L \bullet B^R_L$ for this configuration, where $B_L$ represents a block composed of $L$ sites, $B^R_L$ is the reflection of $B_L$. $\bullet$ represents a single site, and the total length of the super-block is $2*L+2$. $B_{L+1}'$ is formed from the left block plus a single site, i.e., $B_L \bullet$. Open boundary conditions are used. The right block and site $\bullet B^R_L$ are only used to help form the density matrix for $B_{L+1}'$. In the construction of the density matrix, the states of $B_{L+1}'$ are traced over.
Figure 2.2: The configuration of blocks used by White for the density matrix calculations [5]. The rectangles represent blocks containing $L$ sites, and the solid circles represent single sites.

The block formed from $B_L \cdot$ is called the system, while the block $\cdot B_R^L$ is called the environment.

Let $|i\rangle$, $i = 1, \ldots, l$ be a complete set of states of the system $B_L \cdot$ and $|j\rangle$, $j = 1, \ldots, n$ be the states of the rest of the system $\cdot B_R^L$.

Once the superblock is diagonalized and its ground state $|\psi\rangle$ determined, then we can write

$$|\psi\rangle = \sum_{i,j} \psi_{ij} |i\rangle |j\rangle,$$

(2.2)

where the coefficients of $\psi_{ij}$ are real and $\sum_{i,j} |\psi_{ij}|^2 = 1$.

Now suppose there is an optimal set of states $|u^\alpha\rangle$, $\alpha = 1, \ldots, n$, $(n < l)$
with

$$|u^\alpha\rangle = \sum_i u_i^\alpha |i\rangle. \quad (2.3)$$

Then the wave function of the superblock can be approximated as

$$|\psi\rangle \approx |\bar{\psi}\rangle = \sum_{a,j} a_{\alpha,j} |u^\alpha\rangle |j\rangle. \quad (2.4)$$

White minimized

$$S = \|\psi\rangle - |\bar{\psi}\rangle^2 \quad (2.5)$$

by varying over all \(a_{\alpha,j}\) and \(u^\alpha\), subject to \(\langle u^\alpha | u^{\alpha'} \rangle = \delta_{\alpha\alpha'}\). Using singular value decomposition [6] of \(|\psi\rangle\), White showed that the optimal set of states \(|u^\alpha\rangle\) are the eigenvectors of the reduced density matrix with the largest eigenvalues. The reduced density matrix of the system as part of the superblock depends on the state of the superblock and is given by

$$\rho_{ii'} = \sum_j \psi_{ij} \psi_{i'j}. \quad (2.6)$$

The eigenvalues of \(\rho\), \(\omega_\alpha = a_\alpha^2\) represent the probability of the system being in the state \(u^\alpha\) with

9
\[ \sum_{\alpha} \omega_{\alpha} = 1. \]  

(2.7)

The eigenvectors of the reduced density matrix \( u^\alpha \) form the rows of the transform matrix \( O \) and each eigenvector represents one basis state in the new truncated basis. Only \( n \) eigenvectors with the largest weights \( a_\alpha \) will be kept and the accuracy of the truncation is measured by the deviation of the sum

\[ P_n \equiv \sum_{\alpha=1}^{m} \omega_\alpha \]  

(2.8)

from unity.

The super-block Hamiltonian matrix \( H_{\text{super}} \) is formed at the first iteration by combining all the sub-matrices together.

To illustrate this further, we redraw the block configuration in Figure 2.2, see Figure 2.3.

Here \( S_l \) and \( S_r \) are the matrix representations of the spins on the two opposite boundary points for block \( B_L \), \( S_L \) and \( S_L' \) are corresponding spins for the mirror reflection of \( B_L \), and \( S_1 \) and \( S_2 \) are two spin 1/2 individual spins between block \( B_L \) and its mirror reflection \( B_L'^R \).
Then the super-block Hamiltonian should be:

\[ H_{\text{super}} = H_{B_L} + H_{B_R} + S_r \cdot S_1 + S_1 \cdot S_2 + S_2 \cdot S_r. \]  (2.9)

As in conventional RG in order to construct the superblock at the next iteration, we need to obtain new matrices for the blocks, and the interactions between the blocks. Using equation 2.2 mentioned in Sec. 2.1, the new matrices for \( B_L \) should be

\[ H'_{B_L} = O H_{B_L} O^T. \]  (2.10)

Similarly the new matrices for \( S_r \) should be

\[ S'_r = O S_r O^T \]  (2.11)

e tc.

The above procedure is iterated until a fixed point has been reached.
Typically this means until the ground state energy $E_0$ has converged to a specified accuracy.

### 2.3 DMRG Algorithm

Following the discussion above, one can set up the DMRG algorithm as follows [5]:

1. Make 4 initial blocks where the first (left) block contains 1 or more site(s), the second and third blocks consist of a single site and the fourth (right) block is a spatial reflection of the first block.

2. Form the Hamiltonian matrix $H_{super}$ for the superblock.

3. Diagonalize $H_{super}$ by a sparse matrix diagonalization method such as Davidson [7] or the Lanczos [8] algorithm (the Lanczos method is used in this thesis) to find the target states $\psi(i_1,i_2,i_3,i_4)$, e.g. the ground state of the superblock.

4. Form the reduced density matrix $\rho$ for the two block system 1-2 using

$$\rho(i_1,i_2; i_1', i_2') = \sum_{i_3,i_4} \psi(i_1,i_2,i_3,i_4)\psi(i_1',i_2',i_3,i_4).$$

5. Diagonalize $\rho$ to find all the eigenvectors $\nu_\alpha$ and eigenvalues $a_\alpha$, discard
all but the largest $m$ eigenvalues and corresponding eigenvectors.

6. Form matrix representations for active spin operators (those on the ends) of the two block system.

7. Generate a new block 1 by changing basis to the $\nu_\alpha$ using the equation

$$H_1'' = O H_1^{12} O^T.$$ Transform operators in step 6 similarly.

8. Replace the old block 1 with the new block 1 and the old block 4 with the reflection of the new block 1.

9. Return to step 2; repeat until convergence is achieved.

The procedure for the DMRG configuration is illustrated in Figure 2.4, where $S_l, S_r, S'_r, S'_r, S_1$, and $S_2$ are defined as in Sec. 2.2, and $S'_l, S'_l, S''_r, S''_r, S''_r$, and $S''_r$ appear in the Hamiltonians for the second and third iterations respectively.

In each iteration step the superblock is enlarged by the two additional sites, whereas the number of basis states is kept fixed. The calculated properties converge to their values in the thermodynamic limit.

A crucial step in the above algorithm is the storage and diagonalization of the superblock Hamiltonian. Apparently the matrix $H_{super}$ consists of $(4m^2)^2$
Figure 2.4: DMRG method in sketched configuration. The individual spin $S_i$ becomes the right spin $S_r$ at the next iteration. The super-block grows two sites per iteration.

elements. Fortunately most of the matrix elements are zero, and only the non-vanishing elements have to be stored. In addition, a matrix which is block diagonal can be diagonalized block by block which is less CPU intensive than diagonalizing the entire matrix at once. In this thesis, to compute the magnetization curve, we only calculate the lowest energy corresponding to a definite magnetization, so that every time only matrix elements corresponding to that magnetization are required.
2.4 Finite Size Algorithm

The above algorithm is the infinite size algorithm. The superblock is iteratively increased. Thus it is designed to calculate quantities in the thermodynamic limit. This algorithm can be extended improving the accuracy for the calculation of properties of a finite system with fixed size $L$. First one uses the infinite size algorithm until the superblock reaches the desired length $L$. In the subsequent iterations a superblock with fixed length is generated out of two sub-blocks with different lengths. If the left block represents a system of $L'$ sites (we choose $L' = L/2$ here), two sites are added and the superblock is completed by connecting a $L - L' - 2$ site block (constructed from the reflection of the $L - L' - 2$ site block obtained previously from the infinite method). The Hamilton matrices and all other necessary operators of the $L - L' - 2$ site system have to be taken from a previous iteration. In each step one constructs the $L$ site superblock whereas the sizes of the sub-block vary from some starting length $L_{\text{min}}$ to $L - L_{\text{min}} - 2$. This procedure, which is called a sweep through the lattice, can be iterated, so that the left sub-block is increased in each step whereas the right part is taken from a previous iteration (the reflection of the corresponding block). The superblock configurations in the different iterations are depicted in the following sketch, see Figure 2.5.
In the first step the infinite size algorithm is used to iteratively enlarge the $2*L_{\text{min}} + 2$ super-block until the desired length $L$ is reached. The remaining steps are part of the finite size algorithm. Step 3 is repeated several times. Usually two or three sweeps are sufficient and the accuracy is not discernibly increased on further sweeps. The gain of accuracy, however, requires a larger runtime due to the additional sweeps and a larger amount of memory. In each
step all operators corresponding to the $L$ site subsystem have to be stored, since they are needed in subsequent iterations to complete the superblock.

2.5 Accuracy Considerations

The overall DMRG error depends crucially on the number of states kept in each iteration and on the system size (number of iterations). Furthermore it depends on the model which is under study, in particular it depends on the range of interactions and on the boundary conditions. Highest accuracy is obtained if the number of connections (interactions) between the block which is renormalized and the rest of the superblock is minimal. In the infinite size algorithm this is due to the fact that the rest of the superblock, the reflected block, is supposed to approximate the rest of the infinite chain. The result with open boundary conditions is superior to that with periodic boundary conditions, because there are two connections between the block and its reflection for the periodic boundary conditions whereas there is only one connection in the case of open boundary conditions.

For the infinite method, at the fixed point of the iteration, the block $B$ represents one-half of an infinite chain. Often it is useful to have results for a finite chain, but this method is not especially accurate in the early iterations.
That is because initially the density matrices used are derived from very small lattices. On the other hand, the finite method works well for finite systems. With the finite method, the initial error is reduced by supplementary sweeps through the system of the desired length.

We used the DMRG method to compute the ground state energy of a 24 site AF spin chain with the number of retained bases \( m = 64 \). We found \( E_0 = -10.45378576040 \) by finite algorithm, and \( E_0 = -10.45378576022 \) by infinite algorithm. Compared to the exact value \( E_{\text{exact}} = -10.45378576041 \), the relative error is of order \( 10^{-12} \) and \( 10^{-11} \) respectively. In Figure 2.6, we show \( \log \left( \frac{\Delta E}{E_{0,\text{exact}}} \right) \) as a function of the system size \( L \) up to \( L = 100 \), with the number of retained bases \( m = 16, 32, \) and 64 respectively, where \( \Delta E = E_{0,\text{finite}} - E_{0,\text{exact}} \) is the difference between the DMRG results with infinite algorithm and the exact results.
Figure 2.6: \( \log \left( \frac{\Delta E}{E_0^{\text{exact}}} \right) \) as a function of the system size \( L \) up to \( L = 100 \), with the number of retained bases \( m = 16 \) (triangles), 32 (circles), and 64 (squares) respectively, where \( \Delta E = E_0^{\text{infinite}} - E_0^{\text{exact}} \) is the difference between the DMRG results with infinite algorithm and the exact results.
3.1 Crystal Structure of CuGeO\textsubscript{3} and Model

As the first inorganic material identified to exhibit a spin-Peierls transition, CuGeO\textsubscript{3} has a structure simpler than previously known organic materials. This makes it an ideal material for studying the spin-Peierls transition.

At room temperature, CuGeO\textsubscript{3} has an orthorhombic structure with lattice parameters $a = 4.81$ Å, $b = 8.47$ Å, and $c = 2.94$ Å, see Figure 3.1 [9]. We may recognize that the structure of CuGeO\textsubscript{3} consists of CuO\textsubscript{2} ribbons connected via GeO\textsubscript{4} tetrahedra. The magnetic properties of CuGeO\textsubscript{3} which are responsible for the spin-Peierls transition arise from spin 1/2 moments of the Cu$^{2+}$ ions.

The dominant magnetic intra-chain coupling between Cu$^{2+}$ moments in CuGeO\textsubscript{3} arises from super-exchange running over the Cu-O(2)-Cu bonds. Although the Cu-O(2)-Cu angle is close to 90° and therefore expected to be
ferromagnetic by the Goodenough-Kanamori-Anderson (GKA) rules [10], side
effects due to the hybridization of O and Ge orbitals lead to a small effective

Figure 3.1: Crystal structure of CuGeO$_3$ [9]. The spin $1/2$ Cu$^{2+}$ chains are along
the $c$ direction. There are two types of O$^{2-}$ ions shown in black (O(2)) and
gray (O(1)).
Figure 3.2: Projection of the CuO$_2$ ribbons in the a/b-c plane [9]. The nearest neighbor super-exchange path is Cu-O(2)-Cu via the angle $\eta \sim 99^\circ$, the next nearest neighbor super-exchange path is Cu-O(2)-O(2)-Cu indicated by the dashed line.

In addition, the Cu-O(2)-O(2)-Cu exchange paths lead to an additional sizeable next-nearest neighbor AF exchange coupling which frustrates the magnetic interaction between the Cu$^{2+}$ spins.

The magnetic inter-chain coupling can be estimated from the dispersion of the magnetic excitations perpendicular to the chains to be an order of magnitude smaller than the intra-chain exchange [12]. So that a 1-d approach for modeling the magnetic properties of CuGeO$_3$ seems to be reasonable.
In Figure 3.2 the projection of the CuO$_2$ ribbons in the a/b-c plane is shown. From this Figure, we could see the nearest neighbor super-exchange path is Cu-O(2)-Cu via the angle $\eta \sim 99^\circ$, the next nearest neighbor super-exchange path is Cu-O(2)-O(2)-Cu indicated by the dashed line.

According to the crystal structure of CuGeO$_3$, we may describe it with a simplified model consisting of spin 1/2 chain with first and second neighbor AF exchange, the Hamiltonian is as following:

\[ \hat{H} = \sum_i [J_1 \vec{S}_i \cdot \vec{S}_{i+1} + J_2 \vec{S}_i \cdot \vec{S}_{i+2}] - H \sum_i S_i^z, \quad (3.1) \]

where $\vec{S}$ is the $S=1/2$ spin operator, $H$ is the magnetic field, $J_1$ and $J_2$ denote the nearest neighbor (intra-chain) and next nearest neighbor (inter-chain) coupling respectively. We define $\alpha = J_2 / J_1$, which denotes the frustration, reflecting the competition between nearest and next nearest neighbor interactions. The last term is the Zeeman energy, which has to be taken into account in presence of an applied external magnetic field. This Hamiltonian has a very simple form, but captures a variety of behaviors induced by the frustration. For different frustration the system will behave quite differently. It has been pointed out by Haldane [13] that the ground state changes from a gapless spin-fluid phase for $\alpha < \alpha_c$ to a dimer phase with a finite gap for
\( \alpha > \alpha_c \). The critical frustration value has been found to be \( \alpha_c = 0.241167 \) [14, 15].

The parameters in the Hamiltonian equation (3.1) are determined from properties of CuGeO\(_3\) at zero magnetic fields. By a fit of the magnetic susceptibility in the U phase (uniform phase, which will be described in Sec. 3.2), both, Riera et al. [16] and Fabricius et al. [17] find that \( J_1 = 160 \text{ K} \) and \( \alpha = 0.35 \) provide a reasonable parameter set. We will use these values in this thesis.

3.2 Spin-Peierls Transition

The spin-Peierls transition is a magneto-elastic transition that occurs in quasi one-dimensional AF materials when the magnetic free energy decrease due to the formation of singlet spin pairs outweighs the increase in lattice free energy occurring as a result of the dimerization of the regular array.

For the occurrence of a spin-Peierls transition, several preconditions are necessary: first of all, a crystal must contain (quasi) one-dimensional AF spin chains of half-integer spin, i.e. the exchange coupling between neighboring spins along one crystal direction has to be much larger than those perpendicular to this direction. Secondly, a finite magneto-elastic coupling is necessary, i.e.
the magnetic energy can be lowered by a spin-Peierls transition, which may be described as follows: below a certain transition temperature $T_{sp}$ the distances between neighboring spins are no longer uniform but alternate. Due to the magneto-elastic coupling this lead to an alternation of the exchange coupling and each pair of the strongly coupled spins form a spin singlet. This so-called dimerization leads to a gain of magnetic energy which over compensates the loss of elastic energy arising from the alternating structural distortion along the spin chains. In this sense, the spin-Peierls transition is a three-dimensional structural phase transition, driven by the one-dimensional magnetism.

From the experimental point of view there are several characteristic features which signal the spin-Peierls transition. Below $T_{sp}$, superstructure reflections can be observed due to the structural distortion leading to the doubling of the unit cell. In addition, there is a drop of the magnetic susceptibility due to the formation of nonmagnetic spin singlet. Finally, $T_{sp}$ shows very characteristic magnetic field dependence.

By measuring the magnetic susceptibility of CuGeO$_3$, Hase first found CuGeO$_3$ exhibits a spin-Peierls transition around 14.0 K in the absence of the magnetic field [1]. The evidence came from the observation of the characteristic exponential vanishing of susceptibilities in all directions at 14.0
Figure 3.3: The magnetic phase diagram of CuGeO$_3$ [18].

K, which indicates neighboring AF Heisenberg chains (Cu$^{2+}$ ion chains) are subject to a spin dimerization. He also observed the magnetization dependence of the transition temperature.

The magnetic phase diagram of CuGeO$_3$ is shown in Figure 3.3, where D, U, and M denote the dimerized, uniform, and magnetic phases respectively. In the
uniform phase, the system can be considered as a uniform linear chain Heisenberg antiferromagnet. Below the spin-Peierls transition temperature $T_{sp}$, spins are in the dimerized phase where they are in a nonmagnetic singlet state with the dimerization of the lattice. When a magnetic field is applied to the system at a temperature below $T_{sp}$, it shows a nonlinear increase of the magnetization at $H_c$. The magnetic phase diagram of CuGeO$_3$ agrees with results of organic spin-Peierls systems very well despite its rather simple structure.
Chapter 4

Magnetization of CuGeO₃

A large fraction of the experimental as well as the theoretical work on spin-Peierls system is dedicated to investigations of properties in external magnetic fields. In this chapter, we will describe the magnetization of the spin-Peierls compound CuGeO₃. In Sec. 1, we present the computation method of the $M-H$ curve. In Sec. 2, we display the $M-H$ curves of 1-d AF Heisenberg chain with different frustration calculated by different methods, and analyze their different behaviors, especially the middle field cusp singularity, and analyze the magnetization of CuGeO₃.

4.1 Calculation Method

In Sec. 3.1, we presented the model Hamiltonian

$$\hat{H} = \sum_i [J_1 \vec{S}_i \cdot \vec{S}_{i+1} + J_2 \vec{S}_i \cdot \vec{S}_{i+2}] - H \sum_i S_i^z,$$

where $\sum_i S_i^z$ is the total magnetization $M$. Then, for a fixed magnetization
\[ E = E(M) - HM, \]  

(4.1)

where \( E(M) \) is the minimum energy for a magnetization \( M \) at zero magnetic

Figure 4.1: \( E - H \) curve.
field. Then for a magnetization $M$, the $E-H$ curve should be a straight line with slope $M$, and from the level crossing, $E(M) = E(M \pm 1)$, one can determine the field at which the magnetization changes from $M$ to $M + 1$.

One can easily show

$$E(M) - E(M \mp 1) = \pm H.$$  \hfill (4.2)

Thus, for a definite magnetization $M$, we have

$$H = E(M) - E(M - 1),$$  \hfill (4.3)

or

$$H = E(M + 1) - E(M).$$  \hfill (4.4)

For each magnetization $M$, there exists a corresponding magnetic field $H$, the $M-H$ curve is thus obtained by connecting these points together.

Then to compute the magnetization curve, first we should compute the minimum energy $E(M)$ for a magnetization $M$ of the $L$ site system, and then obtain the magnetization curve by determining the level crossing point from $E(M)$ and $E(M \pm 1)$.
4.2 \textbf{M–H Curve}

The magnetization process (\(M–H\) curve, \(M\) : magnetization, \(H\) : magnetic field) of AF spin chain exhibits various phase transition-like behaviors: e.g., the critical phenomena \(\Delta M \sim \sqrt{H-H_c}\) associated with the gapped excitation (excitation gap \(\propto H_c\)) [19, 20] or with the saturated magnetization (at the saturation field \(H_s\)) [20], and the first order transition. There also exists the middle field cusp singularity (MFCS) in the \(M–H\) curve. This cusp singularity appears at \(H = H_{cusp}\) in the middle field region \((H_c < H_{cusp} < H_s)\). The existence of this type of singularity was first demonstrated by Parkinson for the problem of the \(S=1\) spin chain with equal Heisenberg and biquadratic exchange [21].

In Figure 4.2, we show the zero temperature magnetization curves for \(\alpha = 0, 1/4\) calculated by Schmidt [22] via the method of Bonner and Fisher [23]. Also shown here is the Bethe ansatz [24] solution on a ring with \(N = 2048\) [22]. In his study, Schmidt showed that for different \(\alpha\), the magnetization curves behave quite differently near saturation, \(H \to H_s\).

\[
M(\alpha = 0, H \to H_s) \to \frac{1}{2} - \frac{1}{\pi} (H_s - H)^{1/2}
\]  (4.5)
\begin{equation}
M(\alpha=1/4, H \to H_s) \to \frac{1}{2} - \frac{1}{2\epsilon_4^{1/4}} (H_s - H)^{1/4}.
\end{equation}

In the first case for the unfrustrated model one has the well known square root behavior first derived in [25]. At \( \alpha = 1/4 \), numerical results favor a quartic root behavior. From Figure 4.2, we could clearly recognize these two different

![Figure 4.2: The zero temperature magnetization curves for \( \alpha = 0, 1/4 \) calculated by Schmidt [22] via the method of Bonner and Fisher [23]. The solid line is the Bethe ansatz [24] solution calculated by Schmidt on a ring with \( N = 2048 \) [24].](image)

Figure 4.2: The zero temperature magnetization curves for \( \alpha = 0, 1/4 \) calculated by Schmidt [22] via the method of Bonner and Fisher [23]. The solid line is the Bethe ansatz [24] solution calculated by Schmidt on a ring with \( N = 2048 \) [24].
behaviors at $H \rightarrow 4$.

Figure 4.3: The $M - H$ curves of a 20 site AF spin chain calculated by exact diagonalization with $\alpha = 0$ (squares), 0.25 (circles), and 0.35 (triangles) respectively.
Figure 4.4(a): Plot of the magnetization per spin, $m$, versus $h/h_s$ for various values of system size $L$, for $\alpha=0$ [26]. The dotted lines show the finite-size results for $L=18$ and 20, which are step functions of $h/h_s$; the midpoints of the vertical and horizontal parts of the steps for $L=18$ and 20 are marked, respectively, by the open and closed circles. The solid lines represent the estimated limiting ($L \to \infty$) magnetization curves.
Figure 4.4(b): Plot of the magnetization per spin, \( m \), versus \( h/h_s \) for various values of system size \( L \), for \( \alpha = 0.3 \) [26]. The dotted lines show the finite-size results for \( L = 18 \) and 20, which are step functions of \( h/h_s \); the midpoints of the vertical and horizontal parts of the steps for \( L = 18 \) and 20 are marked, respectively, by the open and closed circles. The solid lines represent the estimated limiting (\( L \to \infty \)) magnetization curves.
In Figure 4.3, we show the $M-H$ curves of a 20 site AF spin chain calculated by exact diagonalization with $\alpha=0$, 0.25 and 0.35 respectively. From this figure, we could see the outline of $M-H$ curves at these three different frustrations. We observe the square root behavior for $\alpha=0$, and the quartic behavior for $\alpha=0.25$, and for $\alpha=0.35$, we see that a cusp appears at $H$ close to 2.0, which we will discuss later.

Shown in Figure 4.4 are $M-H$ curves obtained by Tonegawa and Harada [26] for 18 and 20 site chains with $\alpha=0$ and $\alpha=0.3$ respectively.

From Figure 4.4, we also observe the square root behavior for $\alpha=0$, and the quartic behavior for $\alpha$ close to 0.25.

In Figure 4.5, we show the zero temperature $M-H$ curves calculated by Okunishi et al. [27] employing the PWFRG (product wave function renormalization group, a variant of DMRG).

In Sec. 3.1, we mentioned that a phase transition occurs at $\alpha_c \approx 0.241167$. For $\alpha<\alpha_c$, the ground state is a gapless spin-fluid phase, for $\alpha>\alpha_c$, it changes to a dimer phase with a finite gap. The difference between the long-range order in the spin-fluid phase and that in the dimer phase has an immediate consequence for the magnetization curve $M(\alpha,H)$. 
Figure 4.5(a): The $M-H$ curves of the zig-zag spin chain calculated by the PWFRG with number of the retained bases $m=30$ for $\alpha=0.1, 0.2,$ and $0.25$.

We saw in Figures 4.2, 4.3, 4.4 and 4.5 that the $M-H$ curves for $\alpha=0.1, 0.2,$ and $0.25$ have no anomaly in the middle field region, however, the $M-H$ curves for $\alpha=0.35, 0.4,$ and $0.5$ have middle field cusp singularities at $H$ close to the saturation field. In his research, Okunishi also showed that for $\alpha=0.6$, the zero temperature $M-H$ curve has two middle field cusp singularities.

Another thing we find is that the saturation fields are close to each other.
Figure 4.5(b): The $M - H$ curves of the zig-zag spin chain calculated by the PWFRG with number of the retained bases $m = 30$ for $\alpha = 0.35$, 0.4, and 0.5. Inset: magnetization of the curves around the cusps [27].

despite the different frustration. That is because the saturation field of a system with a competing interaction from both the first and the second neighbors in 1-d antiferromagnets is determined mainly by the first neighbor one. Tonegwa and Harada [26] calculated the saturation field of the 1-d isotropic spin $1/2$ Heisenberg antiferromagnet with AF first and second neighbor interactions.

According to their result, the correction of the saturation field by the second
neighbor interaction is very small even in the case of the significantly larger second neighbor interaction in the calculation of Riera and Dobry. However, the quantitative estimation of the second neighbor contribution is difficult from the present experimental data alone, without a satisfactory theory of the magnetization curve for a spin Peierls system with first and second neighbor interactions.

Also we find for small frustration, there exists a linear relation between \( M \) and \( H \) for small external fields \( H \). For \( \alpha \approx 0.5 \), however, a non-vanishing magnetization demands that the external fields exceeds a critical value \( H_c(\alpha) \).

It has been shown that the zigzag chain has fascinating \( M - H \) curves as varying \( \alpha \). What causes this? Below are Okunishi’s explanations. Okunishi argued that this problem can be treated as a spinless Fermi gas, where the Fermions correspond to flipped spins in a ferromagnetic background. This system then is completely characterized by the one Fermion excitation energy dispersion \( \omega(k) \).
Figure 4.6: The dispersion curve of the one-down-spin for the zigzag spin chain [27].

The one-down-spin excitation energy \( \omega(k) \) is calculated to be

\[
\omega(k) = \cos k - 1 + \alpha(\cos 2k - 1),
\]

which we depict in Figure 4.6. This one-particle dispersion curve fully characterizes the qualitative property of the \( M - H \) curve near the saturation field \( H_s \). For \( \alpha \leq 0.25 \), \( \omega(k) \) have a single minimum at \( k = \pi \), while, for \( \alpha > 0.25 \), \( \omega(k) \) has a local maximum at \( k = \pi \) and two minima at
\[ k = \pi \pm \cos^{-1}[1/(4\alpha)]. \] Thus for \( 0 \leq \alpha \leq 0.25 \), the \( M-H \) curve is smooth in the whole field range \( 0 \leq H \leq H_s \). While for \( \alpha > 0.25 \), a "van Hove singularity" corresponding to the double minimum shape of \( \omega(k) \) gives a simple explanation of the middle field cusp singularity in the higher field region of the \( M-H \) curve.

In Okunishi's study, the \( M-H \) curve is obtained from

\[
M = 1/2 - \frac{1}{2\pi} \int R(k)dk, \quad (4.8)
\]

\[
E(M) = \frac{1}{2\pi} \int \omega(k)R(k)dk, \quad (4.9)
\]

\[
H = \frac{\partial E(M)}{\partial M}, \quad (4.10)
\]

where \( R(k) \) is the zero-temperature Fermi distribution function which is unity inside the Fermi vacuum but is zero outside. Therefore, how the particles fill the energy band tells us the essential behavior of the \( M-H \) curve.

Near \( H_s \), the system for \( \alpha \leq 0.25 \) is a Fermi liquid. So that for \( \alpha > 0.25 \), we may expect that the system continues to behave as a Fermi liquid. Qualitatively, the Fermi-liquid character explains the \( M-H \) curve well, in particular, the appearance of the middle field cusp singularity. For quantitative
discussion, however, there emerges an important difference from the case of $\alpha \leq 0.25$: Due to the double minimum shape of $\omega(k)$, the system becomes a two component liquid (each component is composed of modes around each minimum). Such a correlated multicomponent system may behave as a non-Fermi liquid, or a Tomonaga-Luttinger (TL) liquid [28], whose typical example is the Hubbard chain [29].

Now let us consider the $M - H$ curve of CuGeO$_3$, using the parameter set $J_1 = 160$ K and $\alpha = 0.35$, the $M - H$ curve will behave like in Figure 4.5(b) with $\alpha = 0.35$, which has a middle field cusp singularity at $H$ close to the saturation field. We could find similar phenomena in Figure 4.3.

Experimentally, the magnetization curve of CuGeO$_3$ was measured in the presence of the ultra high magnetic field up to 500 T by Nojiri [30]. Nojiri noticed that the experimental magnetization curve shows good agreement with the theoretical curve obtained for the spin 1/2 uniform Heisenberg AF chain with nearest neighbor coupling $J_1 = 183$ K. However, as discussed in Riera and Dobry [16], this model does not satisfactorily reproduce the magnetic susceptibility data. We show in Figure 4.7 the magnetization $M$ versus applied magnetic field $H$ obtained by Riera and Koval [29] with the model proposed in Riera and Dobry for $N = 14$ site chain at $T = 5$ K and 8 K. Here
Figure 4.7: $M - H$ curves calculated by Riera et al. at different temperatures [29]. The theoretical results for $N = 14$ are plotted with lines and the experimental data from Nojiri et al. with symbols [30].

The numerical curves present the typical steplike structure due to the finite lattices involved. We observe an overall good agreement of the theoretical curve compared to the experiment results. Riera and Koval also pointed out that obtained the value of the saturation field that they found ($\approx 253$ T) is in
reasonable agreement with the experimental result [29].

To summarize, in this chapter we have studied the zero temperature magnetization process ($M - H$ curve) for AF spin systems in one dimension. This magnetization process exhibits various phase transition behavior. Near the saturation field, there exists the middle field cusp singularity for $\alpha > 1/4$, and the associated two component Tomonaga-Luttinger liquid behavior is observed, where the dispersion curve of the elementary excitation is the double-well curve. At just $\alpha = 1/4$, the $M - H$ curve behave as $\Delta M \sim (H - H_s)^{1/4}$ unlike the usual square-root behavior in $\alpha < 1/4$.

One thing we should note is that the essential mechanism for appearance of the middle field cusp singularity is the multi-minimum structure of the low lying excitation energy. Such structure may well be expected for systems with non trivial spatial structures and/or competing interactions, which often accompany incommensurability in physical quantities. In fact, the cusp transition for $\alpha < 0.7$ mentioned above is described as the transition between the one and two component Tomonaga-Luttinger (TL) liquid [27]; the two component TL liquid is realized below the lower cusp and/or above the upper cusp reflecting the two chain nature of the system, while the middle field branch still consists of the one component TL liquid.
Chapter 5

Conclusion

As the first inorganic spin-Peierls compound, CuGeO$_3$ has attracted much attention. In this thesis we are mainly concerned about its magnetization process, because the $M - H$ curve exhibits a variety of interesting behavior.

In chapter 2, the density matrix renormalization group method is described. The crystal structure of CuGeO$_3$ and the model Hamiltonian are presented in chapter three. In the fourth chapter, magnetization curves of one dimensional AF Heisenberg chain with different frustration are compared, and their different nature is analyzed.

To summarize, in this thesis, we have studied the zero temperature magnetization process for AF spin system in one dimension, especially CuGeO$_3$. We found this magnetization process exhibits various phase transition behavior. Near the saturation field, there exists the middle field cusp singularity for $\alpha > 1/4$, and the associated two component Tononaga-Luttinger liquid behavior is observed, where the dispersion curve of the elementary excitation is the
double-well curve. At $\alpha=1/4$, the $M-H$ curve behaves as $\Delta M \sim (H - H_s)^{1/4}$ unlike the usual square-root behavior in $\alpha<1/4$. The essential mechanism for appearance of the middle field cusp singularity is the multi-minimum structure of the low lying excitation energy.

In the case of CuGeO$_3$, using the parameter set $J_1=160$ K and $\alpha=0.35$, the $M-H$ curve has a middle field cusp singularity at $H$ close to the saturation field.

In the future, we plan to calculate the $M-H$ curve of CuGeO$_3$ by DMRG method, which can be modeled as an $S=1/2$ AF Heisenberg spin chain with $J_1=160$ K and $\alpha=0.35$. The expected $M-H$ curve for CuGeO$_3$ should be like Figure 4.5(b) with $\alpha=0.35$. 

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Bibliography


