Quantum theory of spin waves for helical ground states in a hollandite lattice

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Abstract
We perform spin-wave analysis of classical ground states of a model Hamiltonian proposed earlier (Mandal et al 2014 Phys. Rev. B 90 104420) for \(\alpha\)-MnO\textsubscript{2} compounds. It is known that the phase diagram of the hollandite lattice (lattice of \(\alpha\)-MnO\textsubscript{2} compounds) consists of four different helical phases (FH, A\textsubscript{2}H, C\textsubscript{2}H, CH phase) in the space of model parameters \(J_1, J_2, J_3\). The spin wave dispersion shows presence of gapless mode which interpolates between quadratic to linear depending on phases and values of \(J_i\). In most cases, the second lowest mode shows the existence of a roton-like minima mainly from \(X(\pi, 0, 0)\) to \(M(\pi, \pi, 0)\) path and it appears at the value of \(k_y = \cos^{-1}\left(\frac{|J_2| + 2|J_3|}{4J_1}\right)\) for constant \(k_x, k_z\). Few higher modes also show similar minima. Each helical phase has its characteristic traits which can be used to determine the phases itself. The analytical expressions of eigenmodes at high symmetry points are obtained which can be utilized to extract the values of \(J_i\). Density of states, specific heat and susceptibilities at low temperature have been studied within spin-wave approximation. The specific heat shows departure from \(T^{1.5(3)}\) dependence found in three-dimensional unfrustrated ferromagnetic(anti-ferromagnetic) system which seems to be the signature of incommensurate helical phase. The parallel susceptibility is maximum for FH phase and minimum for CH phase at low temperature. The perpendicular susceptibility is found to be independent of temperature at very low temperature. Our study can be used to compare experiments on magnon spectrum, elastic neutron scattering, and finite temperature properties mentioned above for clean \(\alpha\)-MnO\textsubscript{2} system as well as determining the values of \(J_i\).

Keywords: spin waves, helical ground states, \(\alpha\)-MnO\textsubscript{2}

(Some figures may appear in colour only in the online journal)

1. Introduction

Magnetic systems having geometrical frustration remain one of the key areas of condensed matter research owing to their ability to produce diverse magnetic phases [1–7] and other quantum many body effects like spin liquids [8–11], fractionalized excitations etc [12–14]. These magnetic systems appear to posses spin magnetic moment (\(s\)) with \(s = 1/2\) to as large as \(s = 2\) in steps of 1/2. The smaller the value of \('s'\), the system bears more quantum effects signifying that classical model is inadequate to describe such system. On the other hand, for large \('s'\), the classical model is often sufficient to describe the system. Though in many cases finding the classical ground states is as difficult as finding its quantum counter part due to frustration arising geometrically or of other origin. Among various naturally existing materials that posses inherent magnetism, various Mn-based compounds are well known for long time [15–18]. Among various Mn-based compounds, various manganese oxides are known for their complex magnetic behaviour. They are also known for their diverse properties for example multiferroics and numerous applications in technology and agriculture. The lattice structures of these various MnO\textsubscript{2} are different and some times the origin of frustration is due to the competing interactions along different bonds. In this
respect, the material $\alpha$-MnO$_2$ which has elementary magnetic moment $s = 3/2$, is noteworthy owing to their similarity with triangular lattice. This particular lattice structure is known as hollandite lattice and this lattice can be constructed out of 3D triangular lattice by selectively removing bonds keeping the 3D character intact [19–21]. One of the main feature of these materials is that the two-dimensional triangular lattices are folded in 3D in a way that a channel-like structure is formed and the diameter of these channels are big enough to accommodate large cations. This property leads to many application [22–25] as electrode materials in batteries, catalyst in oxygen reduction reactions etc.

The earlier studies on these particular MnO$_2$ was mainly confined to experiments which showed that these materials possess different magnetic phases depending on temperature as well as impurity concentration. For example, the experimental investigation in [26] on K$_{1.5}$MnO$_3$O$_{16}$ resulted in three different phase transitions. First one (at temperature near 175 K–215 K) is a charge ordering transition of Mn$^{4+}$ & Mn$^{3+}$ coupled with the ordering of impurities (K$^+$ in this case) in the channels. The second one (near temperature 52 K) is paramagnetic to ferromagnetic transition resulting in a ferromagnetic state which persists up to temperature near 20 K where a third transition occurs by disappearance of the ferromagnetic order. It was also seen that there was a finite susceptibility at 0 K. This strongly suggest that after the third transition, the system enters into some helical magnetic structural phase. The works [27, 28] on $\alpha$–K$_{x}$Mn$_3$O$_{16}$ shows divergences in both zero field cooled and field cooled susceptibilities and noticeable hysteresis for 0.10 $\leq$ $x$ $\leq$ 0.15. However for 0.15 $< x < 0.17$ the sample behaves anti-ferromagnetically with Néel temperature around 25 K. These works also show the presence of spin glass phases [27, 28].

Recently, theoretical models have been prescribed [29, 30] in order to understand the magnetism in $\alpha$-MnO$_2$ system. In [29] an Ising model has been proposed on hollandite lattice which included three different coupling constants $J_{i,d} = 1, 2, 3$ due to their geometrical/orientational differences. This simple model was successful to produce some key feature of the magnetism in hollandite lattice for example (i) the result of frustration and classically degenerate ground state manifold and (ii) the existence of four different collinear magnetic phases (namely A2-AFM, C-AFM, FM, C2-AFM) depending on the sign and magnitude of coupling constants. This simple model also predicts the existence of a spin-glass phase in the presence of impurity or defect in agreement with earlier experiments. In [30], the Ising model were replaced by a 3D Heisenberg model as the $\alpha$-MnO$_2$ materials do not show any particular preferential direction of spontaneous magnetization. This Heisenberg model on hollandite lattice improved some of the results of Ising model for example it established the presence of four different helical ground states in the model parameter space. It may be mentioned that earlier study suggests that helical ground state may be the possible ground state for some materials [26]. The calculated ratio of parallel and perpendicular susceptibility at zero temperature agrees well with experiments. Given the important advancement made in the above mentioned theoretical studies on possible magnetic phases in certain $\alpha$-MnO$_2$ materials, we look for low energy spin-wave excitations and its consequences at low but finite temperature specific heat and susceptibilities. Spin-wave spectrum or excitation is an important physical process which can easily be experimentally determined in elastic neutron scattering experiments. Given the rich classical magnetic phase diagram of hollandite lattice, we think our studies will be important in further determining the true magnetic nature of the $\alpha$-MnO$_2$ materials. Our plan of presentation is the following. In section 2, we describe the classical ground states found in the relevant parameter space as found in the earlier study and define the Holstein–Primakoff (H–P) transformation [31] for evaluating spin-wave spectrum. In section 3, we discuss the magnon-spectrum in detail for each phases. The density of states for magnon and finite temperature specific heat are described in sections 4 and 5 respectively. The finite temperature susceptibility study is done in section 6 and we end up the article with discussion in section 7.

2. Preliminaries: hollandite lattice and classical ground states and spin-wave Hamiltonian

In figure 1, we schematically showed lattice structure of hollandite lattice. In actual material, each lattice site needs to be replaced by Mn-atoms having a tetrahedral structure with O-atoms at the corner of tetrahedra. Figure 1(a) shows the projection of the lattice in x-z plane and figure 1(b) shows a three dimensional view where three different colors have been used to describe three different kind of bonds utilized in the Heisenberg model on hollandite lattice. A given unit cell consists of eight sites as indicated in figure 1. This unit cell is repeated in x-z planes and as well as in y-direction. Each lattice site is connected by two $J_1$-type bonds in y-direction and we can call this $J_1$-chains. Two neighbouring $J_1$ chains are connected by either $J_2$-bonds or $J_3$ bonds. Thus the hollandite lattice can be visualized as $J_1$ – $J_2$ ladders inter-connected by $J_3$ bonds or $J_1$ – $J_2$ ladders interconnected by $J_2$ bonds. For easy description, we generically call the $J_1$ chains containing odd-sub-lattice (even-sub-lattice) as $\alpha$ ($\beta$) chains with $i = 1, 2, 3, 4$. Thus we are having four $\alpha$-chains and four $\beta$-chains along y-direction. The relation of the subscripts ‘i’ of the $\alpha$/$\beta$ chains to that of sub-lattice index ‘k’ is the following. For $\alpha$ chain $i = (2k - 1)$ and for $\beta$ chain $i = 2k$. In an unit cell all the $\alpha$-sub-lattices are in same plane and all the $\beta$-sub-lattices are in other plane shifted by constant displacement in ‘y’ direction. The triangular ladder structure along the channel is the origin of geometrical frustration and non-trivial ordered phases in this system. The classical Heisenberg model on hollandite lattice yields various helical ground states depending on the signs and strength of $J_1$’s. In the classical model $J_1$ has always been taken anti-ferromagnetic as the ferromagnetic choice renders the magnetic ground states trivial as no frustration builds up in the system in this case. For various values and magnitudes of $J_2$ and $J_3$, the magnetic ground states can be collinear or helical. There are four type of collinear or helical structures and they are called C-type (when $J_2$ and $J_3$ are both AFM), C2-type (when $J_2$ is FM and $J_3$ are AFM), FM structure (when $J_2$ and $J_3$ are both FM) and A2-type
AFM (when \( J_2 \) is AFM and \( J_3 \) FM). Various different kind of AFM phases differ from each other by mutual relative orientation among \( \alpha \) (or \( \beta \)) chains as described below and shown in figure 2. To describe it we denote the ground state spin configuration of \( \alpha_1 \) and \( \beta_1 \) chains by \( S_{\alpha_1} = S \) and \( S_{\beta_1} = T \). Then various magnetic ground states can be explained as follows.

- **CH-type** Here the spin configuration of all \( \alpha \) chains are parallel to each other, i.e. \( S_{\alpha_1} = S_{\alpha_2} = S_{\alpha_3} = S \). Similarly for \( \beta \)-chains \( S_{\beta_1} = S_{\beta_2} = S_{\beta_3} = S_{\beta_4} = T \). The angle between spins in \( \beta \) and \( \alpha \) chains are \( \phi, \phi = 0, \pi \) for collinear phase. Here \( S_{\alpha} \) (\( S_{\beta} \)) denotes the spin configuration of \( i^{th} \) \( \alpha \) (\( \beta \)) chains as whole.

- **A2H-type** Here alternative \( \alpha \)-chains are anti-parallelly aligned implying \( S_{\alpha_1} = S_{\alpha_3} = S = -S_{\alpha_2} = -S_{\alpha_4} \). Similar arrangements repeat for \( \beta \) chains.

- **C2H-type** This one repeats the spin-configurations of A2H-type with the difference that while \( \alpha \) chains repeats the orientations of A2H-type, the \( \beta \) chains are rotated by \( \pi \) in \( x-z \) plane relative to A2H-type \( \beta \) chains.

- **FH-type** This one repeats the spin-configurations of CH-type with the difference that while \( \alpha \) chains repeats the orientations of CH-type, the \( \beta \) chains are rotated by \( \pi \) in \( x-z \) plane relative to CH-type \( \beta \) chains.

The above description signifies that one can write down the spin configuration of a given \( \alpha \) chain (say for \( \alpha_1 \)) and a given \( \beta \) chain (say \( \beta_1 \)) to describe the ground state spin-configuration according to the definition given above. In below we write down the ground state configuration of this \( \alpha - \beta \) chains as follows, for hollandite lattice this constitutes a \( J_1 - J_3 \) ladder as shown in figure 3. In CH phase, the ground state configuration can be written as

\[
\vec{S}_{m,\alpha} = s \left( \vec{s} \cos 2m \phi + \vec{z} \sin 2m \phi \right)
\]

\[
\vec{S}_{m,\beta} = s \left( \vec{s} \cos (2m + 1) \phi + \vec{z} \sin (2m + 1) \phi \right).
\]

Here the index ‘\( m \)’ indicates the atomic sites and \( \phi \) is the screw angle. Now we are in a position to perform H–P transformations [31] for the classical ground states described above. To perform the H–P transformation for such non-collinear magnetic ground state it is useful to have a relation between the local (denoted by \( (x’, y’, z’) \)) and global or laboratory coordinate system (denoted by \( (x, y, z) \)) where the quantization direction of a given spin defines the \( x’ \)-axis (which coincides with local spin alignment) of local co-ordinate system. The local and global co-ordinate system is connected via a rotation in \( x-z \) plane as described below.

\[
\begin{bmatrix}
S’_{m,i}\alpha \\
S’_{m,j}
\end{bmatrix}
= 
\begin{bmatrix}
\cos \psi_i & -\sin \psi_i \\
\sin \psi_i & \cos \psi_i
\end{bmatrix}
\begin{bmatrix}
S_{m,i}\alpha \\
S_{m,j}
\end{bmatrix}.
\]

Here \( i = \alpha, \beta \) and \( \psi_\alpha = 2m \phi \) and \( \psi_\beta = (2m + 1) \phi \).

The spin component \( S’_{m,i}\alpha \) is defined as usual,

\[
S’_{m,\alpha}(\alpha/\beta) = s - a_{m,\alpha}(\alpha/\beta) a_{m,\alpha}(\alpha/\beta)
\]

\[
S’_{m,\alpha}(\alpha/\beta) = \sqrt{\frac{\lambda}{2}} \left( a_{m,\alpha}(\alpha/\beta) + a_{m,\alpha}(\alpha/\beta) \right)
\]

\[
S’_{m,\alpha}(\alpha/\beta) = i \sqrt{\frac{\lambda}{2}} \left( a_{m,\alpha}(\alpha/\beta) - a_{m,\alpha}(\alpha/\beta) \right).
\]

Where \( a_{m,\alpha}(\alpha/\beta) \) & \( a_{m,\alpha}(\alpha/\beta) \) represents creation and annihilation operator for magnon at \( m \)th site in \( \alpha \) & \( \beta \) chain respectively. The Heisenberg model on the hollandite lattice can be written as

\[
J_1 \sum_{<i,j>} S_i \cdot S_j
\]

\[
J_2 \sum_{<i,j>} S_i \cdot S_j
\]

\[
J_3 \sum_{<i,j>} S_i \cdot S_j
\]
Our Hamiltonian has two parts, firstly it contains the interactions between nearest neighbour $\alpha$ and $\beta$ chains within a unit cell (intra-cell interaction) and secondly there are inter-cell interaction due to $J_1 - J_3$ ladders which connect a unit cell with neighbouring unit cells. After substituting the ground state ansatz for different phases as described before and implementing equations (1)–(3), we obtain the final Hamiltonian in momentum space as given below,

$$H = \sum_{k=1}^{3} \sum_{(i,j)} \chi_k^\dagger M_k \chi_k + \text{(constant terms)} \quad (4)$$

where the basis is given below,

$$\chi_k = [\chi_{1,k}, \chi_{2,k}]^T$$

$$\chi_k \equiv [a_k^{\dagger,1,\alpha_1}, a_k^{\dagger,1,\alpha_2}, a_k^{\dagger,1,\beta_1}, a_k^{\dagger,1,\beta_2}] \quad (6)$$

$$\chi_{2k} = [a_k^{\dagger,1,\alpha_1}, a_k^{\dagger,2,\alpha_1}, a_k^{\dagger,1,\beta_1}, a_k^{\dagger,2,\beta_1}]$$

and the coefficient matrix $M_k$ is a $(16 \times 16)$ matrix. The detailed expressions of $M_k$ for different phases have been given in the appendix. Below we describe the magnon spectrum obtained from the above Hamiltonian.

### 3. Spin-wave spectrum

The spectrum of the Hamiltonian in equation (5) is found following [32, 33] which involves diagonalization of dynamical matrix obtained by equation of motion method. It may be mentioned that diagonalization of quadratic bosonic Hamiltonian is a non-trivial problem of itself owing to its different commutation relations than its fermionic counter part. For a quadratic fermionic Hamiltonian an unitary transformation (often obtained from diagonalizing Hamiltonian matrix for fermion system) automatically guarantees the fermionic commutation relation. However for bosonic system this is not always true and one needs different strategy to diagonalize the system. The interested reader may refer to [32, 33] for further information. The spin-wave spectrum obtained for hollandite lattice is quite rich and bear different characteristic signatures of different helical phases. In figure 4, we plot the dispersion along high symmetry points, $\Gamma(0,0,0)$, $X(\pi,0,0)$, $M(\pi,\pi,0)$, $Z(0,0,\pi)$, $R(\pi,0,\pi)$ and $A(\pi,\pi,\pi)$. In all the phases we see the presence of acoustic as well as optical modes. However, one needs to be cautious to use the phrase ‘acoustic mode’ as though it is gapless and starts at the center of Brillouin zone (0,0,0), due to the helical angle $\phi$ which is not zero, the dispersion is not linear always. Such acoustic branches has been termed as quasi-acoustic branches in recent studies [34]). Also the appearance of roton minima in the second lowest band in the magnon dispersion is one of the remarkable feature of the spectrum. As the different phases has unique characteristic feature we prefer to describe the dispersion for different phases separately which will facilitate to have a comparative picture of all the phases.

#### 3.1. FH-phase

We begin our discussion with FH-phase which seems to be a good starting point to compare all other phases. In this phase there is a gapless quadratic mode at $\Gamma$ points which extends upto $X$ point. The other prominent feature of this phase is the existence of eight non-degenerate bands (for the path $\Gamma$ to $X$ point) which are symmetrical in regard to the touching points of fourth and fifth bands. This unique feature is not repeated in other phases. From $X$ to $M$, the bands become doubly degenerate and all bands converge at $M$ points. In between $M$ to $Z$, the bands become non-degenerate but again converge at four almost equidistant eigenvalues. Form $Z$ to $R$, they are mostly four doubly degenerate bands which monotonously converge at a given eigenvalue at $A$ point.

#### 3.2. A2H-phase

Now we turn to A2H phase. We remind that A2H phase differs from FH phase such that the alternative $\alpha$ chains are now alternatively antiferromagnetically arranged. Similar thing happens for $\beta$ chains. This AFM alignment reflects in the fact that the gapless mode at $\Gamma$ points become more linear as clear from the second from right panel of figure 4. This feature continues for CH and C2H phase as well where there are some anti-ferromagnetic arrangements between different $\alpha$ (or $\beta$) chains. The other notable feature is that at $X$, $Z$ and $R$ points the eight eigenvalues meet at three separate points only. The band width i.e. the energy difference between the highest to lowest band also decreases compared to FH phase.

#### 3.3. C2H-phase

The main characteristic feature of C2H phase is that the band width further decreases compared to A2H phase. However while in A2H phase there are three distinct eigenvalues at $Z$...
and $R$ point, in C2H phase there are two low energy eigenvalue and two high energy eigenvalue separated by a large gap appears. The acoustic mode at $M$ point represented by red plot also becomes four-fold degenerate while in A2H phase and FH phase it is two-fold degenerate.

3.4. CH-phase

In CH-phase the band width is the minimum among all the four phases. However a unique characteristics is that the bands are symmetric for the path $X \rightarrow M$ and $R \rightarrow A$. Also the eigenvalues are closely spaced than all other phases. In the appendix we have given the Hamiltonian for different phases which can be used to get the spectrum for different phases. From the material point of view this is very useful in the sense that one can use those formulas and play with various values of $J_1$ to match the experimental magnon spectrum. Further in appendix B, we have given the exact expression for energy at specific symmetry point mainly at $\Gamma$, $X$ and $R$ point which can be used to compare with experimental data obtained from elastic neutron scattering.

Also note that the excitation energies are eight-fold degenerate at $M(\pi, \pi, 0)$ point. At this point the Hamiltonian contains only those terms which are related to individual chains and other inter chain coupling terms are not present, i.e. spin deviations are distributed along 'y' direction only and no modes are available along $x$ and $z$ direction at this point. The ground state configurations are identical for all individuals chains. It may be the reason behind the same excitation energies for fluctuations around $k_y = 2\phi$ in all modes and all phases at this point. Excitation energy at this point is given by $\epsilon_{\mu}(k = (0, \pi, 0)) = S\sqrt{(E_{GS} + 1)(E_{GS} + 1)\cos 2\phi}$ (where $E_{GS}$ is the ground state energy per site as obtained in the previous study using classical Heisenberg model [30]) and we have checked that this is same whenever $k_y = \pi$ irrespective of $k_x$ and $k_z$ (i.e. $\epsilon_{\mu}(k_x, \pi, k_z) = \epsilon_{\mu}(0, \pi, 0)$) as we can see at $A(\pi, \pi, \pi)$ points in the dispersion curves of figures 4 and 5.

Before we close the discussion we would like to mention that appearance of roton-like minima in the magnon dispersion is quite general for this hollandite lattice. They mainly appear along the path of $X$ to $M$, $M$ to $Z$ and $R$ to $A$ points. Historically roton-minima refers to the presence of a minima in the dispersion superfluid He at finite non-zero momenta [35]. This is distinctly different from the gapless linear(phonon-like) excitation that appears near the zero momenta. Often the roton-minima is attributed to the interactions among the Bogoliubov quasi-particles [36], long range interactions [37] etc. Later various other system not pertaining to superfluid He-2 has also shown this kind of local minima in the dispersion at finite momenta. The examples range from cold-atomic system [41, 37], fractional quantum-Hall system [38-41] etc. As clear from the spin-wave dispersion of the hollandite system in comparison to the spin-wave dispersion of a single ladder [42] from figures 4 and 5, the roton-like minima origonates from the interactions between the spin-wave excitations between neighboring chains and also owes to the long range correlation that exists due to the underlying helical order. We have observed that the roton minima appears for a path on which $k_y$ varies having non-zero values of $k_x$, $k_z$. The value of $k_y$ for which the
roton minima appears turns out to be \( k_y = \cos^{-1} \left( \frac{|J_1|+|J_2|}{4|J_1|} \right) \) for the path \( X(\pi, 0, 0) \rightarrow M(\pi, \pi, 0) \). The fact that a non-zero value of \( k_y \) is needed for the roton minima to appear denotes that the interactions between Bogoliubov modes of connected chains are necessary ingredient for roton minima to exist. In figure 5, we have denoted the spectrum for hollandite lattice chains are necessary ingredient for roton minima to exist. In (b), spectrum is shown for \( J_2 = 0 \) which reduces the hollandite lattice to disconnected channel like structure. The spin-wave spectrum contains four bands owing to four \( J_1 \) and \( J_2 \) chains extending to \( \pi \)-direction. The spin-wave spectrum represented by blue plot in (b) appears for both signs of \( J_2 \) and is doubly degenerate for each sign. In (c), we have repeated the plots of (a) and additionally plotted the spectrum for \( J_2 = 0 \) and \( J_1 = \pm 1 \) for which the spin-wave spectrum bear characteristics of simple AFM or FM represented by blue and dashed blue plots respectively.

4. Density of magnon modes

Now we briefly describe the profile of the density of states of different phases. The density of states is defined as the \( \text{Tr}(\text{Im}G(E)) \) where the Green function \( G(E) \) is obtained from \( G_{\alpha \alpha'}(k, \sigma) \) in the following way,

\[
G_{\alpha \alpha'}(k, \sigma) = \langle T_{\sigma} a_{k, \alpha}(\sigma) a_{k', \alpha'}^\dagger(0) \rangle_{\alpha' \in \{\alpha, \beta\}}
\]

\[
G_{\alpha \alpha'}(k, i\omega_n) = \int_0^\beta e^{i\omega_n\sigma} G_{\alpha \alpha'}(k, \sigma) d\sigma
\]

where the Matsubara bosonic frequency, \( \omega_n = \frac{2\pi n}{\beta} \). Once the imaginary time Green function is determined, the retarded Green function can be obtained by a replacement \( i\omega_n \rightarrow \omega + i\eta \). The density of states is obtained as,

\[
D(E) = -\sum_{\alpha, \beta}^{\alpha=1,4} \int \frac{dk}{N\pi} \text{Im} \langle G_{\alpha \alpha'}(k, E) + G_{\beta \beta'}(k, E) \rangle.
\]

Figure 6 represents the plots for density of magnon modes in arbitrary unit for few parameter values. The plots shows that for low energy the density of states is vanishingly small due to the presence of low energy gapless mode which is constraint to have one dimensional character. The first peaks near \( E = 1 \) is due to appearance of first gapped mode as evident from figure 4. The largest peaks in density of states appears near \( E = 2.25 \) which is related to the excitations of \( M \) point energy. A decrease of gap can be observed when we apply magnetic field for a particular choice of point in the phase diagram, see figure 6(d). We also notice that for FH phase we have finite density of states at comparatively high energy and it gradually decreases for A2H, C2H and CH phases. The density of states profile in conjunction with the dispersion spectrum described in earlier section will be useful for determination of a particular phase.

5. Low temperature specific heat

The total energy \( E(T) \) at a given temperature \( T \) can be written as \( E = \sum_{j} \epsilon_{i,j}(n_{i,j}(T)) \). Where \( (n_{i,j}(T)) \) is the B–E distribution function and \( \epsilon_{i,j} \) is the energy for a given mode \( j \) and wave vector \( k \). This allows us to write the expression of specific heat as given below,
6. Study of susceptibilities

In this section we will study the effect of external magnetic field on the helical ground states. First we consider the case where the magnetic field is applied in the plane of polarization.

\[ C(T) = \frac{1}{k_B T^2} \sum_{k, \mathbf{k}, \mathbf{k'}, j} \frac{\epsilon_k^2 e^{\beta \epsilon_k}}{(e^{\beta \epsilon_k} - 1)^2} \]  \hfill (11)

In the second line of the above equation, we have converted the momentum summation to the integral over energy which is scaled by \( J_1 \) i.e. \( T \rightarrow \frac{T}{J_1} \). The above relation for specific heat due to magnon contribution depends on temperature as \( T^{9/8} \) and the temperature exponents decreases (increases) when we decrease (increase) coupling strengths. Figure 9 shows very low temperature dependence of specific heat in other phases. The temperature exponent is decreasing as we go from \( CH \rightarrow C2H \rightarrow A2H \rightarrow FH \), i.e. specific heat is increasing. This is because at very low temperature lowest energy mode gives most of the contributions. This lowest energy modes are more available when we go from \( CH \rightarrow C2H \rightarrow A2H \rightarrow FH \) (see dispersion curves and density of state curves discussed in previous sections). In the next section we analyse our results for low temperature susceptibilities for magnetic field applied parallel and perpendicular to the plane of polarization.

Figures 7–9 represent the low temperature dependence of specific heat due to magnon contribution. The noticeable characteristic of these curves is that they exhibit anomalous peaks known as Schottky anomaly [43, 44]. We expect this peaks for a system having gap and it appears when thermal energy reaches the gap. Figure 7 shows that the Schottky peak shifts towards higher temperature which is due to the increase of gap with the increase of coupling strengths. The figure 7(b) also contains the specific heat plots for four similar points \((|J_2/J_1|, |J_3/J_1|) = (1, 1)\) in the phase diagram [30] which shows that for a given set of model parameters, the peaks appear at same temperature though the peak height gradually decreases from \( FH \rightarrow A2H \rightarrow C2H \rightarrow CH \) phase. Though at higher temperature the crossover of specific heat happens among various phases due to the detail changes of profile of density of states. It may be noticed that the peak height is decreasing in phases other than \( CH \) phase due to reduction in peak height in density of state curves which points to the fact that in \( CH \) phase the energy bands are closely spaced than other phases as evident from figure 4. It is also instructive to compare the temperature dependence of heat capacity at very low temperature for hollandite system with other known magnetic system. For example, at very low temperature an unfrustrated collinear ferromagnet and anti-ferromagnet, the magnon contribution to specific heat depends on temperature as \( T^{3/2} \) and \( T^0 \) respectively [45]. Figure 8 shows the low temperature dependence of specific heat in \( CH \) phase for different \((J_2/J_1, J_3/J_1)\) in phase diagram. The magnon contribution to specific heat depends approximately on temperature as \( T^{9/8} \) and the temperature exponents decreases (increases) when we decrease (increase) coupling strengths. Figure 9, shows very low temperature dependence of specific heat in other phases. The temperature exponent is decreasing as we go from \( CH \rightarrow C2H \rightarrow A2H \rightarrow FH \), i.e. specific heat is increasing.

In the next section we analyse our results for low temperature susceptibilities for magnetic field applied parallel and perpendicular to the plane of polarization.

Figure 6. Density of magnon modes in (a) all phases for \( |J_2| = |J_3| = J_1 \), (b) all phases for \((J_2/J_1, J_3/J_1) = (0.7, 0.6)\), (c) \( CH \) phase for different \((J_2/J_1, J_3/J_1)\), (d) \( CH \) phase for different field for \( |J_2| = |J_3| = J_1 \).
of the ground state spin configuration and in second case the magnetic field is applied perpendicular to the plane of polarization. For our case, the plane of polarization of ground state spin configuration is x-z plane and without loss of generality we can take the magnetic field to be along x-axis. Below we provide the details of susceptibilities for parallel magnetic field.

6.1. Magnetic field parallel to the plane of spin polarization

The Hamiltonian in the presence of magnetic field applied along x-axis is given below,

\[ H_{||} = H - \sum S_i \alpha h. \]  

In the above \( H \) represents the Hamiltonian given in equation (4) and magnetic field is assumed to be \( \vec{h} = h \vec{e}_x \). The detailed steps of arriving at the expression of susceptibilities is given in appendix C. Here we give the outline. In the first step, we apply the definition of spin operators as given by equation (3) to the Hamiltonian in equation (13). After the above substitution, the second term in equation (13) yields both quadratic and linear terms. First the quadratic terms are taken into account with \( H \) and diagonalized. Then the linear terms are re-expressed in the diagonalized basis. After a translation of the diagonalized basis by a constant terms, the linear terms can be absorbed to obtain the total energy. The diagonalized basis has the following form (with a displacement in \( k \) as \( k \to k - \phi \) to maintain the same positive and negative eigenvalues):

\[
\begin{pmatrix}
T_{11} & T_{12} & \ldots & T_{18} \\
T_{21} & T_{22} & \ldots & T_{28} \\
\vdots & \vdots & \ddots & \vdots \\
T_{81} & T_{82} & \ldots & T_{88}
\end{pmatrix}
\]

(14)

The induced magnetization, \( M_1 \) can be written as, \( M_1 = \langle S^x \rangle = M_1 + M_2 \) where \( M_1 \) contains the quadratic terms and \( M_2 \) contains the linear terms. After a straightforward evaluation we obtain the following expressions for \( M_1 \) and \( M_2 \) as follows.

\[
M_1 = -\frac{1}{2} \sum_{k_j} \langle n_{k_j} \rangle C_j
\]

(15)

\[
M_2 = \sqrt{\frac{1}{2}} \sum_{j=1}^{8} \sum_{\phi} \frac{1}{\epsilon_{\phi}} p_j p^*_j \delta_{k,\phi}
\]

(16)

where \( C_j = t_{1j} t^*_{j,1} + e^{-i\phi} t_{2j} t^*_{j,2} + \text{h.c.} \) and \( t \)-elements form the unitary transformation matrix that transforms \( \{\alpha \} \)-basis to diagonalized \( \{\beta \} \)-basis and the bosonic distribution function, \( n_{k_j} = \frac{1}{\epsilon_{\phi_{k_j}} + 1} \).

Figure 10 represents the magnetic susceptibility plots for \( J_1 = J_2 = J_3 \), indicating a low temperature magnetic ordering which persists up to some temperature and finally vanishes after further increase in temperature. This results are also qualitatively supported by experimental results [26–28]. Figure 11 shows the magnetic susceptibility for different field (a) and for different coupling strengths in CH phase (b). As expected we notice that for FH phase the magnetic susceptibility is maximum and gradually decreases as we go to A2H, C2H and CH phase.

6.2. Magnetic field perpendicular to plane of spin polarization

Now we describe the effect of magnetic field having direction perpendicular to the plane of polarization, in our case this implies that the magnetic field is applied in y-direction. The second term in the Hamiltonian in equation (13) changes to \( H_{\perp} = -\frac{1}{2} \sum_{\alpha, \beta} S_{\alpha, \beta} \). In Fourier space this can be written as,

\[
H_{\perp}' = \gamma \sum_{ij} \left( a_i^\dagger a_{\alpha j} + a_{\alpha j} a_i^\dagger \right) ; \alpha, \beta \in \alpha_j.
\]

(17)

Therefore total Hamiltonian in diagonalized basis can be written as,
many unusual characteristics for example the existence of gapless modes which can be either linear or quadratic depending on phases. This seems to be characteristics of Helical phases. The second lowest modes shows existence of roton minima for a large region of parameter spaces and it is found that roton minima appears at the degenerate value of $k_z$ for which the classical energy is minimum for disconnected chains. Few of the higher modes also shows the roton minima. Each classical phases has its own characteristics which can be useful in determining a particular phases. The analytical expressions of eigenvalues at high symmetry point can be used to determine the $J_i$ values. The finite temperature property for example specific heat and susceptibility shows behavior similar to one dimensional system but the exact dependency on temperature differ from usual AFM/FM system. Our extensive study can be useful to compare with future experimental results and do further analysis for helical magnetism.

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Appendix A

The magnon Hamiltonian has following form,

$$M_k = s \begin{bmatrix} A(k) & B(k) \\ B(k)^* & A(k) \end{bmatrix}.$$  \hspace{1cm} (A.1)

In the above we have dropped the constant terms. The $A(k)$ and $B(k)$ are $8 \times 8$ matrix whose expression is given below. For magnetic field applied parallel to the plane of polarization, the full coefficient matrix (with $k_1 = (k_x, k_y, \phi, k_z)$, and $k_2 = (k_x, k_y, \phi, k_z)$ where $k_x, k_y, k_z$ are the components of ‘$k$’ along three principal axes) is the following,

$$M_{k, h} = s \begin{bmatrix} A(k_1) & F & B(k_1) & 0 \\ F^* & A(k_2) & 0 & B(k_2) \\ B(k_1) & 0 & A(k_1) & F \\ 0 & B(k_2) & F^* & A(k_2) \end{bmatrix}.$$  \hspace{1cm} (A.2)

where the basis,

$$\chi_k = [\chi_{1,k_1}, \chi_{1,k_2}, \chi_{2,k_1}, \chi_{2,k_2}]^T$$

$$\chi_{1,k} = [a_{k_x,\alpha_1} \cdot a_{k_y,\alpha_2} \cdot a_{k_z,\beta_1} \cdot a_{k_z,\beta_2}]$$

$$\chi_{2,k} = [a_{-k_x,\alpha_1} \cdot a^+_{-k_y,\alpha_2} \cdot a^+_{-k_z,\beta_1} \cdot a^+_{-k_z,\beta_2}]$$

where $i = 1, 2$. Before giving the expression of $A, B$ matrix, we write the independent element which is found in $A, B$,

$$a(k) = J_1 \frac{1}{2} [(1 + \cos 2\phi) \cos k_y - 2 \cos 2\phi]$$

$$- (J_2 + 2|J_3|) \cos \phi,$$  \hspace{1cm} (A.5)

$$b(k) = \frac{1}{2} J_1 (1 - \cos 2\phi) \cos k_y,$$  \hspace{1cm} (A.6)
\[ d_2(k) = \frac{1}{2} J_1(1 + \cos \phi) \cos \frac{k_y}{2} e^{-ik_z}, \quad (A.7) \]
\[ d_3(k) = \frac{1}{2} J_1(1 + \cos \phi) \cos \frac{k_y}{2} e^{-ik_z}, \quad (A.8) \]
\[ e_2(k) = \frac{1}{2} J_2(1 - \cos \phi) \cos \frac{k_y}{2} e^{-ik_z}, \quad (A.9) \]
\[ e_3(k) = \frac{1}{2} J_1(1 - \cos \phi) \cos \frac{k_y}{2} e^{-ik_z}, \quad (A.10) \]
\[ d_m(k) = \frac{1}{2} J_3(1 + \cos \phi) \cos \frac{k_y}{2} e^{-i(k_x - k_y)/2}, \quad (A.11) \]
\[ d_p(k) = \frac{1}{2} J_3(1 + \cos \phi) \cos \frac{k_y}{2} e^{i(k_x + k_y)/2}, \quad (A.12) \]
\[ e_m(k) = \frac{1}{2} J_3(1 - \cos \phi) \cos \frac{k_y}{2} e^{-i(k_x - k_y)/2}, \quad (A.13) \]
\[ e_p(k) = \frac{1}{2} J_3(1 - \cos \phi) \cos \frac{k_y}{2} e^{i(k_x + k_y)/2}, \quad (A.14) \]
\[ f_m(k) = \frac{1}{2} J_3(1 + \cos \phi) \cos \frac{k_y}{2} e^{-i(k_x - k_y)/2}, \quad (A.15) \]
\[ f_p(k) = \frac{1}{2} J_3(1 + \cos \phi) \cos \frac{k_y}{2} e^{i(k_x + k_y)/2}, \quad (A.16) \]
\[ g_m(k) = \frac{1}{2} J_3(1 - \cos \phi) \cos \frac{k_y}{2} e^{-i(k_x - k_y)/2}, \quad (A.17) \]
\[ g_p(k) = \frac{1}{2} J_3(1 - \cos \phi) \cos \frac{k_y}{2} e^{i(k_x + k_y)/2}, \quad (A.18) \]
\[ h_1 = h/2, \quad h_2 = \hbar e^{i\theta}/2. \quad (A.19) \]

**A.1. For CH phase**

\[
A(k) = \begin{bmatrix}
    a & d_2 & 0 & 0 & d_m & 0 & d_p & e_2 \\
    d_2^* & a & d_3 & 0 & 0 & g_p^* & 0 & 0 \\
    0 & d_3 & a & d_2 & 0 & g_m & 0 & 0 \\
    d_m^* & 0 & d_2^* & a & d_3^* & 0 & 0 & 0 \\
    0 & 0 & 0 & d_3 & a & d_2 & 0 & d_p \\
    0 & g_p & 0 & 0 & d_3 & a & d_2 & 0 \\
    d_p^* & 0 & 0 & 0 & d_p^* & 0 & d_p^* & a \\
\end{bmatrix}
\quad (A.20)
\]

\[
F = \begin{bmatrix}
h_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & h_2 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & h_1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & h_2 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & h_1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & h_2 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & h_2 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & h_1 \\
\end{bmatrix}
\quad (A.25)
\]

**A.2. For C2H phase**

\[
B(k) = \begin{bmatrix}
b & e_2 & 0 & e_m & 0 & 0 & 0 & e_3 \\
e_2^* & b & e_3^* & 0 & 0 & 0 & f_p^* & 0 \\
0 & e_3 & b & e_2 & 0 & f_m & 0 & 0 \\
e_m^* & 0 & e_2^* & b & e_3^* & 0 & 0 & 0 \\
0 & 0 & 0 & e_3 & b & e_2 & 0 & e_p \\
0 & 0 & f_m^* & 0 & e_2^* & b & e_3^* & 0 \\
e_3^* & 0 & 0 & e_p & 0 & e_2^* & b & e_3 \\
\end{bmatrix}
\quad (A.21)
\]

\[
A(k) = \begin{bmatrix}
a & e_3 & 0 & 0 & e_m & 0 & d_2 \\
e_3^* & a & d_2 & 0 & e_p & 0 & 0 & 0 \\
0 & d_2 & a & e_3 & 0 & f_m & 0 & 0 \\
e_m^* & 0 & e_2^* & a & d_3^* & 0 & 0 & 0 \\
0 & 0 & e_3 & a & d_2 & 0 & f_p & 0 \\
0 & e_p & 0 & d_2 & a & e_3 & 0 & 0 \\
e_p^* & 0 & 0 & e_3^* & a & d_2^* & 0 & 0 \\
d_2^* & 0 & f_m & 0 & 0 & e_3^* & b & d_3 \\
\end{bmatrix}
\quad (A.26)
\]
\[
B(k) = \begin{bmatrix}
    b & d_3 & 0 & 0 & 0 & d_m & 0 & e_2 \\
    d_3^* & b & e_2^* & 0 & d_p^* & 0 & 0 & 0 \\
    0 & e_2 & b & d_3 & 0 & 0 & 0 & g_m \\
    0 & 0 & d_3^* & b & e_2^* & 0 & g_p^* & 0 \\
    0 & d_p & 0 & e_2 & b & d_3 & 0 & 0 \\
    d_m^* & 0 & 0 & d_3^* & b & e_2^* & 0 & g_p^* \\
    0 & 0 & 0 & g_p & 0 & e_2 & b & d_3 \\
    e_2^* & 0 & g_m^* & 0 & 0 & 0 & d_3^* & b
\end{bmatrix}
\]

(A.27) \hspace{1cm} \begin{bmatrix}
    b & d_3 & 0 & 0 & 0 & d_m & 0 & d_2 \\
    d_3^* & b & d_2^* & 0 & d_p^* & 0 & 0 & 0 \\
    0 & d_2 & b & d_3 & 0 & 0 & 0 & g_m \\
    0 & 0 & d_3^* & b & d_2^* & 0 & g_p^* & 0 \\
    0 & d_p & 0 & d_2 & b & d_3 & 0 & 0 \\
    d_m^* & 0 & 0 & d_3^* & b & d_2^* & 0 & g_p^* \\
    0 & 0 & 0 & g_p & 0 & d_2 & b & d_3 \\
    d_2^* & 0 & g_m^* & 0 & 0 & 0 & d_3^* & b
\end{bmatrix}
\]

(A.30)

\[
F = \begin{bmatrix}
    h_1 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & -h_2 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & -h_1 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & h_2 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & h_1 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & -h_1 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & h_2
\end{bmatrix}
\]

(A.28) \hspace{1cm} \begin{bmatrix}
    h_1 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & -h_2 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & -h_1 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & h_2 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & h_1 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & -h_1 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & -h_2
\end{bmatrix}
\]

(A.31)

A.4. FH phase

\[
A(k) = \begin{bmatrix}
    a & e_3 & 0 & 0 & 0 & e_m & 0 & e_2 \\
    e_3^* & a & e_2^* & 0 & e_p^* & 0 & 0 & 0 \\
    0 & e_2 & a & e_3 & 0 & 0 & 0 & f_m \\
    0 & 0 & e_3^* & a & e_2^* & 0 & f_p^* & 0 \\
    0 & e_p & 0 & e_2 & a & e_3 & 0 & 0 \\
    e_m^* & 0 & 0 & e_3^* & a & e_2^* & 0 & 0 \\
    0 & 0 & 0 & f_p & 0 & e_2 & a & e_3 \\
    e_2^* & 0 & f_m^* & 0 & 0 & 0 & e_3^* & a
\end{bmatrix}
\]

(A.29)

Appendix B. Symmetry point eigenvalues

B.1. CH phase

\begin{itemize}
    \item \Gamma-point energies:
        \[0, \sqrt{(a \pm j_2d)^2 - (b \pm j_2e)^2}, \]
        \[\sqrt{(a \pm (j_2 - 2j_3)d)^2 - (b \pm (j_2 - 2j_3)e)^2}, \]
        \[\sqrt{(a - (j_2 + 2j_3)d)^2 - (b - (j_2 + 2j_3)e)^2}. \]
    \item X-point energies:
        \[\sqrt{(a \pm j_2d)^2 - (b \pm j_2e)^2}, \sqrt{a^2 - b^2 + (d^2 - e^2)(j_2^2 + 4j_3^2)} \pm 2\sqrt{(ad - be)^2(j_2^2 + 4j_3^2)}. \]
\end{itemize}

B.2. C2H phase

\begin{itemize}
    \item \Gamma-point energies:
        \[0, \sqrt{(a \pm j_2e)^2 - (b \pm j_2d)^2}, \sqrt{(a - j_2e)^2 - (b - j_2d)^2 - 4j_3(ad - be - j_3(d^2 - e^2))}, \]
        \[(a \pm j_2e)^2 - (b \pm j_2d)^2 \mp 4j_3(ad - be - j_3(d^2 - e^2)). \]
    \item X-point energies:
        \[\sqrt{a^2 - b^2 - (d^2 - e^2)(j_2^2 - 2j_3^2) - 2j_3(ad - be) \pm \sqrt{2(d^2 - e^2)(2j_3^2(be - ad) + (d^2 - e^2)j_3^2(-j_2^2 + j_3^2)) + j_3^2(ad - be)^2 + j_3^2(ae - bd)^2}}, \]
        \[\sqrt{a^2 - b^2 - (d^2 - e^2)(j_2^2 - 2j_3^2) + 2j_3(ad - be) \pm \sqrt{2(d^2 - e^2)(2j_3^2(ad - be) + (d^2 - e^2)j_3^2(-j_2^2 + j_3^2)) + j_3^2(ad - be)^2 + j_3^2(ae - bd)^2}}, \]
\end{itemize}
\[ R\text{-point energies:} \]
\[ \sqrt{(a \pm J_2 e)^2 - (b \pm J_3 d)^2}, \]
\[ a^2 - b^2 + (d^2 - e^2)(-J_2^2 + 4J_3^2) \pm 2\sqrt{(ae - bd)J_2^2 + 4J_3^2(ad - be)^2 - 4J_2^2J_3^2(d^2 - e^2)}. \]

B.3. A2H phase

- \( \Gamma\)-point energies:
\[ \sqrt{(a \pm J_2 d)^2 - (b \pm J_2 e)^2}, \sqrt{(a - J_2 d)^2 - (b - J_2 e)^2 - 4J_3(ae - bd + J_3(d^2 - e^2))}, \]
\[ (a \pm J_2 d)^2 - (b \pm J_2 e)^2 + 4J_3(ae - bd + J_3(d^2 - e^2)). \]

- \( X\)-point energies:
\[ a^2 - b^2 + (d^2 - e^2)(J_2^2 - 2J_3^2) - 2J_3(ae - bd)\pm \]
\[ 2\sqrt{(d^2 - e^2)(2J_3^3(ae - bd) + (d^2 - e^2)J_3^2((-J_2^2 + J_3^2)) + J_3^2(ad - be)^2 + J_3^2(ae - bd)^2)} \]
\[ a^2 - b^2 + (d^2 - e^2)(J_2^2 - 2J_3^2) + 2J_3(ae - bd)\pm \]
\[ 2\sqrt{(d^2 - e^2)(2J_3^3(bd - ae) + (d^2 - e^2)J_3^2((-J_2^2 + J_3^2)) + J_3^2(ad - be)^2 + J_3^2(ae - bd)^2)}. \]

- \( R\)-point energies:
\[ \sqrt{(a \pm J_2 e)^2 - (b \pm J_2 d)^2}, \]
\[ a^2 - b^2 + (d^2 - e^2)(J_2^2 - 4J_3^2) \pm 2\sqrt{(ad - be)J_2^2 + 4J_3^2(ae - bd)^2 - 4J_2^2J_3^2(d^2 - e^2)}. \]

B.4. FH phase

- \( \Gamma\)-point energies:
\[ \sqrt{(a \pm J_2 e)^2 - (b \pm J_2 d)^2}, \sqrt{(a - J_2 e)^2 - (b - J_2 d)^2 - (a - (J_2 + 2J_3)d)^2}. \]

- \( X\)-point energies:
\[ a^2 - b^2 - (d^2 - e^2)(J_2^2 + 2J_3^2) - 2J_3(ae - bd)\pm \]
\[ 2\sqrt{(J_3(d^2 - e^2) + (ae - bd))((J_2^2 + J_3^2))} \]
\[ a^2 - b^2 - (d^2 - e^2)(J_2^2 + 2J_3^2) + 2J_3(ae - bd)\pm \]
\[ 2\sqrt{(J_3(d^2 - e^2) - (ae - bd))((J_2^2 + J_3^2))}. \]

- \( R\)-point energies:
\[ \sqrt{(a \pm J_2 d)^2 - (b \pm J_2 e)^2}, \sqrt{a^2 - b^2 + (d^2 - e^2)(J_2^2 + 4J_3^2) \pm 2\sqrt{(ad - be)^2(J_2^2 + 4J_3^2)}}. \]

In each phase Z-point has same energies as X-point has. In each case M-point has energy \( \sqrt{(J_1 + E_{GS})(J_1 \cos 2\phi + E_{GS})} \)
where \( a = \frac{1}{2}(1 - \cos 2\phi) - |J_3| + 2|J_3| \cos \phi, b = \frac{1}{2}J_1(1 - \cos 2\phi), \]
\( d = \frac{1}{2}(1 + \cos \phi), e = \frac{1}{2}(1 - \cos \phi), \) and \( E_{GS} = J_1 \cos 2\phi + (|J_2| + |J_3|) \cos \phi. \)
Appendix C. Derivation of susceptibilities

For a single ladder and with field direction lying on the plan of polarization (say, x-direction):
for α-chain the perturbing Hamiltonian is

\[ H'_\alpha = - \sum_m h S^z_{m,\alpha} \]

\[ = -h \sum_m \left( \cos (2m\phi) S^z_\alpha - \sin (2m\phi) S'^z_\alpha \right) \]

\[ = \frac{h}{2} \sum_k \left( a^\dagger_k a_{k+2\alpha,\alpha} + a^\dagger_k a_{2\alpha,\alpha} a_k \right) \]

\[ - \frac{h}{2} \sqrt{\frac{\pi}{2}} \left( a^\dagger_{2\alpha,\alpha} - a^\dagger_{-2\alpha,\alpha} + a_{2\alpha,\alpha} - a_{-2\alpha,\alpha} \right). \quad (C.1) \]

Similarly for β-chain this Hamiltonian can be derived by replacing \( 2m\phi \) by \( (2m+1)\phi \), i.e., \( H'_\beta = (H'_\alpha)_{2m\phi \rightarrow (2m+1)\phi} \). Therefore,

\[ H'_\beta = - \sum_m h S^z_{m,\beta} \]

\[ = -h \sum_m \left( \cos ((2m+1)\phi) S'^z_\beta - \sin ((2m+1)\phi) S'^z_\beta \right) \]

\[ = \frac{h}{2} \sum_k \left( e^{i\alpha} a^\dagger_{k,\beta} a_{k+2\beta,\beta} + e^{-i\alpha} a^\dagger_{k,\beta} a_{2\beta,\beta} a_k \right) \]

\[ - \frac{h}{2} \sqrt{\frac{\pi}{2}} \left( e^{-i\alpha} a^\dagger_{2\beta,\beta} - e^{i\alpha} a^\dagger_{-2\beta,\beta} \right) \]

\[ - \frac{h}{2} \sqrt{\frac{\pi}{2}} \left( e^{i\alpha} a_{2\beta,\beta} - e^{-i\alpha} a_{-2\beta,\beta} \right). \quad (C.2) \]

The quadratic terms in the perturbing Hamiltonian can be absorbed in the free Hamiltonian and that can be diagonalized using a transformation of the basis (equation (13)) (with a displacement in \( k \) as \( k \rightarrow k - \phi \) to maintain the same positive and negative eigenvalues). With the new basis we can write the remaining perturbing terms as:

\[ H'/\left\{ \frac{h}{2} \sqrt{\frac{\pi}{2}} \right\} = a^\dagger_{2\beta,\beta} a_{2\beta,\beta} + e^{-i\alpha} a^\dagger_{2\beta,\beta} a_{2\beta,\beta} a_{-2\beta,\beta} \]

\[ + e^{-i\alpha} a^\dagger_{-2\beta,\beta} a_{2\beta,\beta} a_{-2\beta,\beta} - e^{i\alpha} a_{-2\beta,\beta} a_{-2\beta,\beta} \]

\[ = \sum_{j=1,4} b^\dagger_{\phi,j} + \sum_{j=5,8} b^{\dagger}_{-\phi,j} q_j. \quad (C.3) \]

Here \( q_j \) = \( (-t'_{\phi,j} + t_{\phi,j} e^{-i\phi} t'_{\phi,j} + e^{i\phi} b_{\phi,j} + \text{h.c.}) \). Now the Hamiltonian in diagonalized basis can be written as:

\[ H = H_0 + H'. \] Where, \( H_0 = \sum_{k,j} t_{k,j} a^\dagger_k b_{j,k} \). In order to remove the linear terms let us make the following transformation: \( b_{k,j} \rightarrow b_{k,j} + p_j \). A very straightforward calculation shows that the linear terms will be completely removed for \( p_j = -\frac{h}{2} \sqrt{\frac{\pi}{2}} \delta_{k,\phi,j} \). Thus the energy correction for the linear terms can be written as:

\[ E' = - \sum_{\phi,j} \frac{1}{2} p_j p_j^* \delta_{k,\phi}. \quad (C.4) \]

Finally let us calculate the magnetization:

\[ M_{||} = \langle S^z \rangle = M_1 + M_2 \]

\[ = -\frac{1}{2} \sum_{k,j} (a^\dagger_k a_{k+\phi,\alpha} + a^\dagger_k a_{k+\phi,\alpha} + a^\dagger_k a_{k+\phi,\beta} a_{k+\phi,\beta} + \text{h.c.}) \]

\[ \Rightarrow M_1 = -\frac{1}{2} \sum_{k,j} \langle n_{k,j} \rangle C_j, \quad (C.5) \]

where \( C_j = t_{1,j} t'_{1,j} + e^{-i\phi} t_{2,j} t'_{2,j} + \text{h.c.} \) and \( t \)-elements form the unitary transformation matrix that transforms \( 'a' \)-basis to diagonalized \( 'b' \)-basis and the bosonic distribution function,

\[ n_{k,j} = \frac{1}{e^{\beta n_{k,j}} - 1}. \quad (C.6) \]

And,

\[ M_2 = \frac{1}{2} \sqrt{\frac{\pi}{2}} \sum_{j=1,8} p_j p_j^* \delta_{k,\phi}. \quad (C.7) \]

All these calculations have been done for a single \( J_1 - J_2 \) (figure 1), we extended this calculation for full hollandite case and found out the magnetic susceptibility curves.

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