Chapter 3

Electronic structure and magnetic properties in spin gap material: \( \text{Sr}_2\text{Cu(BO}_3\text{)}_2 \)

Low dimensional quantum spin systems continue to enjoy considerable attention both theoretically as well as experimentally due to the wealth of fascinating properties exhibited by them.\(^{(1)}\) These systems exhibit a rich variety of phases due to the enhanced quantum fluctuations in reduced dimensionality. Of particular importance are systems that exhibit spin gap.\(^{(2)}\) Exotic features related to the ground state and excitations of such gapped systems form a subject matter of current interest. After the discovery of high \( T_c \) superconductivity in two-dimensional cuprates, the copper based compounds have had a special focus. In this respect Cu based borates also attracted considerable attention. In particular, the quasi two dimensional spin \( S = 1/2 \) compound \( \text{SrCu}_2\text{(BO}_3\text{)}_2 \)\(^{(3)}\) was suggested to be the experimental realization of the Shastry-Sutherland\(^{(4)}\) model exhibiting spin gap behavior and magnetization plateaus at 1/8, 1/4 and 1/3 of the saturated magnetization. Following this discovery, there have been attempts to tune the magnetic couplings in such systems upon proper substitutions in order to explore the rich phase diagram of the Shastry Sutherland model. One such attempt has been the realization of \( \text{CdCu}_2\text{(BO}_3\text{)}_2 \) by replacement of \( \text{Sr}^{2+} \) by another divalent cation \( \text{Cd}^{2+} \).\(^{(5)}\) This compound exhibits long range magnetic order and 1/2 magnetization plateau. A recent theoretical work\(^{(6)}\) uncovers that \( \text{CdCu}_2\text{(BO}_3\text{)}_2 \) is a possible realization of the spin 1/2 decorated anisotropic Shastry-Sutherland lattice.

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In this Cu based borate family, the magnetic properties of the recently discovered spin gap compound \( \text{Sr}_2\text{Cu} (\text{BO}_3)_2 \) is particularly intriguing.\(^7\) The structure of \( \text{Sr}_2\text{Cu} (\text{BO}_3)_2 \) consists of \( \text{CuO}_2 \) square plaquettes and \( \text{CuO}_6 \) octahedra which are connected to each other by \( \text{BO}_3 \) triangular units and run along the crystallographic \( c \) direction as illustrated in Fig. 3.1. Although this composition is very similar to the Shastry-Sutherland\(^4\) compound \( \text{Sr}_2\text{Cu} (\text{BO}_3)_2 \),\(^8\) but it has a very different magnetic lattice and the high field and low temperature magnetic behavior is particularly interesting. The magnetization data\(^7\) for \( \text{Sr}_2\text{Cu} (\text{BO}_3)_2 \) at low field is consistent with the fact that the material has a singlet ground state comprising dimers, with intra-dimer coupling \( J \approx 100 \text{ K} \). As expected in the presence of higher applied field, the triplet excitations are observed. Interestingly, the applied field where excitation of singlet into triplet takes place, is found to be significantly smaller than that predicted for isolated dimers. This in turn indicated that the inter-dimer couplings may be important and possibly responsible for the triplet states at smaller fields. The importance and the nature of the inter-dimer couplings are not always obvious from the structural considerations. It is therefore important to establish a connection between the underlying chemical complexity of the compound and the corresponding spin lattice. In this context \textit{ab initio} electronic structure calculations have played an important role in analyzing and understanding such low dimensional quantum spin systems.\(^9\text{-}^{12}\)

In this chapter, we shall examine the electronic structure of \( \text{Sr}_2\text{Cu} (\text{BO}_3)_2 \) in some detail and in particular identify the dominant exchange paths and the relevant spin Hamiltonian. This spin Hamiltonian will be employed to compute the magnetic susceptibility as a function of temperature and magnetization both as a function of magnetic field as well as temperature using Quantum Monte Carlo simulation (stochastic series expansion).\(^{13\text{-}15}\) We shall compare our results with available experimental data, in order to clarify the importance of the inter-dimer coupling as anticipated in the experiments. The remainder of this chapter is organized as follows: in section 3.1 we discuss the crystal structure and the computational details. Section 3.2 is devoted to the analysis of the electronic structure, derivation of the relevant spin Hamiltonian and its solution using the QMC method. Finally the summary and conclusions
3. Electronic structure and magnetic properties in spin gap material: \textit{Sr}_2\textit{Cu}(\textit{BO}_3)_2 are given in section 3.3.

### 3.1 Crystal Structure and Computational details

\textit{Sr}_2\textit{Cu}(\textit{BO}_3)_2 exists in two structural phases. The high temperature $\beta$-\textit{Sr}_2\textit{Cu}(\textit{BO}_3)_2 phase studied here, crystallizes in the orthorhombic space group \textit{Pnma} with the lattice parameter $a = 7.612 \, \text{Å}$, $b = 10.854 \, \text{Å}$, $c = 13.503 \, \text{Å}$.(16) All the electronic structure calculations in the present work are carried out using the lattice parameters and the atomic positions as reported in Ref. 16. The structure of \textit{Sr}_2\textit{Cu}(\textit{BO}_3)_2 is shown in Fig. 3.1. The unit cell has 8 formula units with 88 atoms in the unit cell as shown in Fig. 3.1(a). It has a layered structure (ac plane), where each layer is built of distorted Cu(I)O$_6$ octahedra, square planar Cu(II)O$_4$ units, and triangular B(1,2,3)O$_3$ units, as shown in Fig. 3.1(b). This distorted Cu(I)O$_6$ octahedron has four inequivalent oxygens O1, O2, O3, and O7 surrounding each Cu(I) ion. Each Cu(I)O$_6$ octahedron is elongated along O1-O2 axis, with distances $d_{\text{Cu(I)-O1}} = 2.42 \, \text{Å}$ and $d_{\text{Cu(I)-O2}} = 2.49 \, \text{Å}$. The equilateral oxygens are at $d_{\text{Cu(I)-O7}} = 1.92 \, \text{Å}$ and $d_{\text{Cu(I)-O3}} = 1.99 \, \text{Å}$. These layers are stacked along the crystallographic b-axis with Sr ions in between them. As can be seen in Fig. 3.1(b), each Cu(I)O$_6$ octahedron is connected to two Cu(I)O$_6$ octahedra and a pair of square planar Cu(II)O$_4$ units with the aid of BO$_3$ triangular units. Among the two square planar units one is connected to the Cu(I)O$_6$ octahedron by a pair of BO$_3$ units and the Cu(I) and Cu(II) residing on the octahedral and square planar unit respectively defines the structural dimer, as indicated in Fig. 3.1(b).

In order to analyze the electronic structure of \textit{Sr}_2\textit{Cu}(\textit{BO}_3)_2 we have carried out density functional calculations within local density approximation (LDA) by employing Stuttgart TB-LMTO-47 code,(17) based on tight binding linearized muffin-tin orbital (TB-LMTO) method in the atomic sphere approximation (ASA). The space filling in the ASA is obtained by inserting appropriate empty spheres in the interstitial regions. For the TB-LMTO-ASA calculation the basis set for the self consistent electronic structure calculation for \textit{Sr}_2\textit{Cu}(\textit{BO}_3)_2 includes Sr \textit{(s, d)}, Cu \textit{(s, p, d)}, O \textit{(s, p)} and B \textit{(s, p)} and the rest are downfolded. A (4x2x2) $k$-mesh has been
3. Electronic structure and magnetic properties in spin gap material: $\text{Sr}_2\text{Cu(BO}_3\text{)}_2$

Figure 3.1: (a) Unit Cell of $\text{Sr}_2\text{Cu(BO}_3\text{)}_2$, (b) One Cu(I) octahedra is connected with two Cu(II)O$_4$ square planar units and two other Cu(I)O$_6$ octahedra. The dimer unit is indicated by the dotted circle.

used for self-consistency. In addition, the total energy calculations necessary for the evaluation of the exchange integrals are carried out in the plane wave basis along with the projected augmented wave (PAW)\(^{(18)}\) method as implemented in the Vienna \textit{ab initio} simulation package (VASP).\(^{(19)}\) The exchange-correlation (XC) term in DFT was treated within the GGA due to Perdew-Burke-Emzerhof (PBE).\(^{(20)}\) We have used a plane-wave energy cutoff of 500 eV and $k$-space sampling on a $4 \times 2 \times 2$ Monkhorst-Pack grid.

In order to derive a low energy effective model Hamiltonian that will serve as the single electron part of the many body Hamiltonian necessary to model the system, we have employed $N^{th}$ order muffin-tin orbital (NMTO) downfolding method.\(^{(21-23)}\) The present $N^{th}$ order muffin-tin orbital (NMTO) code is not self-consistent, so we have used the current Stuttgart TB-LMTO-ASA code to generate the LDA potentials. The basis set used in LMTO-ASA method is small and localized. This method is simple and highly efficient due to the atomic sphere approximation (ASA) which takes the one-electron potential and charge density to be spherically symmetric inside space filling Wigner-Seitz (WS) spheres whose overlap is neglected. For close-packed symmetric structures, this approximation to the potential is very
3. Electronic structure and magnetic properties in spin gap material: Sr$_2$Cu(BO$_3$)$_2$

good. However, for open structures with low symmetry (low-dimensional structures, i.e., layered or chain compounds) it is difficult to find good ASA and the important details of the potential are neglected. For this type of materials, a full-potential scheme is often necessary for an accurate description of the electronic structure. The TB-LMTO ASA code can be employed to obtain band dispersions with the accuracy comparable to full potential calculations by suitable choice of empty spheres. We have employed such an approach for the study of Sr$_2$Cu(BO$_3$)$_2$. However there is an alternative approach using the overlapping muffin-tin approximation (OMTA). In the Appendix A we shall illustrate OMTA method to obtain the band dispersion for 1D spin chain compound Sr$_2$Cu(PO$_4$)$_2$ with the accuracy comparable to the full potential calculation.

A strong on-site Coulomb interaction ($U$) is added to the non-interacting Hamiltonian obtained from the NMTO downfolding method to construct a Hubbard model for the many body description of Sr$_2$Cu(BO$_3$)$_2$. This model in the limit of half filling reduces to the Heisenberg model and thereby provides the necessary spin Hamiltonian. The resulting spin Hamiltonian has been solved to calculate susceptibility as a function of temperature and magnetization as a function of temperature and magnetic field using QMC with the aid of stochastic series expansion (SSE) algorithm.$^{(13-15,24)}$

3.2 Results and Discussions

3.2.1 Electronic structure and low energy model Hamiltonian

The non spin polarized band structure for Sr$_2$Cu(BO$_3$)$_2$ obtained by TB-LMTO ASA method is shown in Fig. 4.16. The bands are plotted along the various high symmetry lines of the Brillouin zone corresponding to the orthorhombic lattice of Sr$_2$Cu(BO$_3$)$_2$. All the energies are measured with respect to the Fermi level of the compound. The characteristic feature of the band structure is the isolated manifold of eight bands crossing the Fermi level ($E_F$) which...
arises from the eight copper atoms in the unit cell. These eight bands are predominantly of Cu-$d_{x^2-y^2}$ character in the local frame of reference where Cu is at the origin and the $x$ and $y$ axis point along the oxygens residing either on the basal plane of the octahedron or the square planar unit. These isolated eight bands are responsible for the low energy physics of the material. These bands are half filled and separated from the low lying O $p$ and other non Cu-$d_{x^2-y^2}$ valence bands by a gap of about 1.8 eV. The system is insulating (see inset of Fig. 4.16) and the magnitude of the gap is calculated to be 10 meV in LDA indicating interactions in the Cu-$d_{x^2-y^2}$ manifold. Fig. 3.3 displays the total DOS and the partial DOS contribution from Cu, B, O, and Sr near the Fermi level. We note that in addition to the Cu and oxygens the bands at the Fermi level has non-negligible admixture with the B states which are expected to participate in the super exchange process. In order to ascertain the accuracy of our ASA calculations we also performed the electronic structure calculation using projector augmented wave (PAW)\(^{(18)}\) method encoded in the Vienna \textit{ab initio} simulation package (VASP).\(^{(19)}\) The
3. Electronic structure and magnetic properties in spin gap material: $\text{Sr}_2\text{Cu}(\text{BO}_3)_2$

Figure 3.3: The total density of states of $\text{Sr}_2\text{Cu}(\text{BO}_3)_2$. Inset shows the partial density of states for O, B, and Sr in the energy range close to $E_F$.

density of states calculated by these two different approaches is found to agree well with each other.

The $N^{th}$ order muffin-tin orbital (NMTO) downfolding method\(^{[21-23]}\) has been established to be an efficient ab initio scheme to construct low energy, few band, tight binding model Hamiltonian. This method generates the basis set which describes an isolated band or group of bands. The low energy model Hamiltonian is constructed by selective downfolding method via integration process. The high energy degrees of freedom are integrated out from the all orbital LDA calculations. The number of energy points ($N$) used for the downfolding technique is very important for the accuracy of the calculation. For an isolated set of bands, atom centered and localized set of Wannier functions may be generated by symmetrical orthonormalization of the NMTOs.\(^{[25]}\)

In order to extract the low energy model Hamiltonian, we have retained the isolated eight band complex near the Fermi level and downfolded the rest with the choice of four energy points $E_0 = -1.6\text{ eV}$, $E_1 = -0.2\text{ eV}$, $E_2 = 1.2\text{ eV}$, and $E_3 = 2.6\text{ eV}$. The downfolded bands in comparison to the all orbital LDA band structure is shown in Fig. 3.4 and we note that the
3. Electronic structure and magnetic properties in spin gap material: $\text{Sr}_2\text{Cu(BO}_3\text{)}_2$

Figure 3.4: Downfolded band structure (shown in red dotted line) compared to the full orbital band structure (shown in black line) for $\text{Sr}_2\text{Cu(BO}_3\text{)}_2$. $E_0$, $E_1$, $E_2$, $E_3$ mark the energy points used in NMTO calculation.

agreement is excellent. The Fourier transform of the low energy Hamiltonian $H_k \rightarrow H_R$ [where $H_R$ is given by, $H_R = \sum_{ij} t_{ij} (c_i^\dagger c_j + h.c.)$] gives the effective hopping parameters between the various Cu atoms. The exchange interactions can be expressed as sum of antiferromagnetic (AFM) and ferromagnetic (FM) contributions $J = J_{\text{FM}} + J_{\text{AFM}}$. For strongly correlated systems, the antiferromagnetic contributions can be calculated by the following relation: $J_{\text{AFM}} = \frac{4t_n^2}{U_{\text{eff}}}$, where $U_{\text{eff}}$ is the effective onsite Coulomb interaction and $t_n$ corresponds to the hopping via superexchange paths. The various hopping integrals ($> 1$ meV) extracted for $\text{Sr}_2\text{Cu(BO}_3\text{)}_2$ are listed in Table A.1 and the notation is indicated in Fig. 3.1.

The various Cu-Cu hoppings in the ac plane (see Fig. 3.1(b)) are primarily mediated via oxygens that are shared by the Cu(I)O$_6$ octahedra, Cu(II)O$_4$ square planar units and the BO$_3$ units. The equatorial oxygens of a Cu(I)O$_6$ octahedron (e.g. O3 and O7) hybridize strongly with the Cu(I)-$d_{x^2-y^2}$ orbital while the apical oxygens (O1 and O2) hardly hybridize with it. As a consequence the effective Cu-$d_{x^2-y^2}$-Cu-$d_{x^2-y^2}$ hopping is strong provided the equatorial oxygens of an octahedron are linked by B either to the oxygens in the square planar unit or to
Figure 3.5: Wannier function of Cu-$d_{x^2-y^2}$, placed at two Cu(II) sites residing on the square planar units. One is connected to the Cu(I)O$_6$ octahedron by a pair of BO$_3$ units (in left) and the other Cu(II) is connected to the Cu(I)O$_6$ octahedron by one BO$_3$ unit (in right). Lobes of orbitals placed at different Cu(II) sites are colored differently.

The equatorial oxygens of a neighboring octahedron. This is precisely the case for the structural dimer thereby accounting for its appreciable hopping, $t_2 = 112$ meV. The hopping $t_3$ and $t_4$ (see Fig. 3.1(b)) proceed with the aid of the apical oxygens and therefore are expected to be small. Our calculations indeed reveal that $t_3$ is negligible and $t_4 \approx 4$ meV. In addition to the above hoppings there is a small direct hopping $t_1$ between a pair of Cu(II) residing on neighboring square planar units, along crystallographic $a$ axis.

Our above argument is further substantiated by a plot of Cu-$d_{x^2-y^2}$ Wannier function, where we have plotted the Cu-$d_{x^2-y^2}$ Wannier function for Cu(II) residing on the square planar unit and connected to the Cu(I)O$_6$ octahedron by a pair of BO$_3$ units. (see Fig. 3.5(left)). The plot reveals that the Cu(II)-$d_{x^2-y^2}$ orbital forms strong $pd\sigma$ antibonds with the neighboring O-$p_x$ and O-$p_y$ orbitals. From the tail of the Wannier function we find that it strongly hybridizes with the BO$_3$ network and also with the Cu(I)-$d_{x^2-y^2}$ orbital. This hybridization mediated by a pair of BO$_3$ units as argued above is responsible for the strong $t_2$ hopping. The plot of Wannier
Table 3.1: Hopping integrals, O-O distance in exchange path and exchange interactions (in meV) are listed here.

<table>
<thead>
<tr>
<th>Hopping path</th>
<th>Cu-Cu distance (Å)</th>
<th>O-O distance (Å)</th>
<th>O-O path</th>
<th>Hopping (meV)</th>
<th>$J_{AFM}^r (t_2/t_2)^2$ for $U = 4$ eV</th>
<th>$J_{AFM}^r + J_{AFM}^F$ for $U = 6$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_1$</td>
<td>4.03</td>
<td>3.39</td>
<td>O5-O6</td>
<td>13.6</td>
<td>0.015</td>
<td>0.45</td>
</tr>
<tr>
<td>$t_2$</td>
<td>4.27</td>
<td>2.37</td>
<td>O6-O7</td>
<td>112.0</td>
<td>1.0</td>
<td>-12.71</td>
</tr>
<tr>
<td>$t_4$</td>
<td>6.12</td>
<td>2.40</td>
<td>O1-O3</td>
<td>4.08</td>
<td>0.001</td>
<td>-0.69</td>
</tr>
<tr>
<td>$t_5$</td>
<td>6.25</td>
<td>3.07</td>
<td>O7-O6</td>
<td>40</td>
<td>0.127</td>
<td>-2.74</td>
</tr>
<tr>
<td>$t_6$</td>
<td>6.35</td>
<td>3.1</td>
<td>O3-O5</td>
<td>9.52</td>
<td>0.007</td>
<td>2.38</td>
</tr>
</tbody>
</table>

function for the Cu(II) which is connected to Cu(I) by a single BO$_3$ unit via the apical oxygen (see Fig. 3.5(right)) reveals that although Cu(II) hybridizes strongly with the BO$_3$ unit but the tail of the Wannier function does not have any weight at Cu(I) site because this hybridization is weak as it proceeds via the apical oxygen thereby accounting for its negligible coupling.

![Figure 3.6: Effective orbital corresponding to the downfolded NMTOs, placed at B(3) site.](image)

In order to clarify the role of B in mediating the strong hopping $t_2$, we have plotted in Fig. 3.6 the Wannier function corresponding to B(3)-$p_z$ in an energy range above the Fermi level belonging to the antibonding part of the B-O hybrid dominated by the B-$p$ states. As expected the plot reveals that B(3)-$p_z$ orbital forms antibonds with the neighboring oxygens in the triangular unit which in turn form an antibonding linear combination with Cul and CuII. The main role of the B is to bring the oxygens together in the BO$_3$ unit and strengthen the
Figure 3.7: Effective orbital corresponding to the downfolded NMTOs, placed at Cu(I) and Cu(II) sites corresponding to the $t_5$ interaction. Lobes of orbitals placed at different Cu sites are colored differently.

Next we have considered the hoppings along the crystallographic $b$-direction particularly $t_5$, which is the second largest interaction. Fig. 3.7 shows the Wannier function plots of Cu-$d_{x^2-y^2}$ corresponding to $t_5$ hopping. From the Wannier function, we gather that the Cu-Cu inter-dimer hopping along $b$ direction primarily proceeds via oxygens. Although the Cu-Cu distance is large, but the relatively strong hopping is due to short O-O distances (see Table A.1) (comparable to van der Waals distance) in the hopping pathway.\(^{(12)}\) This hopping path will be responsible for the inter-dimer exchange interaction.

Table A.1 reveals that the dominant hoppings (> 10 mev) are $t_1$, $t_2$, and $t_5$. However a tight binding (TB) analysis reveals that excluding $t_1$ a reasonable fit to the low energy NMTO band structure is obtained except for the small splitting along ($\Gamma$ X), (S Y) and (R T) directions (see
3. Electronic structure and magnetic properties in spin gap material: $\text{Sr}_2\text{Cu(BO}_3\text{)}_2$

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**Figure 3.8**: The plot of band structures calculated by tight binding analysis using $t_1$, $t_2$, and $t_5$ hopping parameters (shown in red dotted line); and $t_1$ and $t_5$ hopping parameters (shown in black line) for $\text{Sr}_2\text{Cu(BO}_3\text{)}_2$.

Fig. 3.8). Using second order perturbation expression $J_{\text{AFM}}^{\text{AFM}} = \frac{\mu_n^2}{U_{\text{eff}}}$, the intra-dimer exchange interaction is calculated to be $12.5 - 10.03 \text{ meV}$, taking the standard value of $U_{\text{eff}} = 4.0 - 5.0 \text{ eV}$. The ratio of the exchange integrals are listed in Table A.1, where we have $J_{5}^{\text{AFM}} = 0.127J_{2}^{\text{AFM}}$, and as expected the other alternation parameters are negligibly small.

In addition, to the above estimate for the AFM contribution to the exchange interactions we have employed a complementary approach to calculate the total exchange interactions. We have performed total energy calculations in the framework of GGA+U$^{(27)}$ method for various ordered spin configurations. In order to extract the various exchange interactions, the relative energies of these ordered spin state determined from the GGA+U calculations, are mapped onto the corresponding energies obtained from the total spin exchange energies of the Heisenberg spin Hamiltonian $H = \sum_{i,j} J_{ij} \hat{S}_i \cdot \hat{S}_j$. The total spin exchange energies of the eight
Table 3.2: The relative energies (in meV) of eight ordered spin states are listed here.

<table>
<thead>
<tr>
<th>$E_i - E_{FM}$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($U = 4 \text{ eV}$)</td>
</tr>
<tr>
<td>$\Delta E_1$</td>
<td>58.5</td>
</tr>
<tr>
<td>$\Delta E_2$</td>
<td>30.0</td>
</tr>
<tr>
<td>$\Delta E_3$</td>
<td>8.9</td>
</tr>
<tr>
<td>$\Delta E_4$</td>
<td>50.5</td>
</tr>
<tr>
<td>$\Delta E_5$</td>
<td>29.3</td>
</tr>
<tr>
<td>$\Delta E_6$</td>
<td>0.4</td>
</tr>
<tr>
<td>$\Delta E_7$</td>
<td>29.6</td>
</tr>
</tbody>
</table>

ordered spin states are expressed as

$$E(FM) = \frac{1}{4}(J_1 + J_2 + J_3 + 2J_5 + 2J_6)$$
$$E(AF1) = \frac{1}{4}(J_1 - J_2 + J_3 - 2J_5 - 2J_6)$$
$$E(AF2) = -\frac{1}{4}J_1$$
$$E(AF3) = \frac{1}{4}(J_1 + J_2 - J_3 + 2J_5 + 2J_6)$$
$$E(AF4) = \frac{1}{4}(-J_1 - J_2 + J_5)$$
$$E(AF5) = \frac{1}{4}(-J_1 + J_6)$$
$$E(AF6) = \frac{1}{4}(J_2/2 - 2J_3 + J_5 - J_6)$$
$$E(AF7) = \frac{1}{4}(-J_1 + J_2 - J_3 - 2J_5 + 2J_6)$$

(3.1)

For the GGA+U calculations the onsite Coulomb interaction ($U$) for Cu is taken to be $U = 4 \text{ eV}$ and $U = 6 \text{ eV}$ and the onsite exchange interaction $J = 1 \text{ eV}$. The calculated energy differences are shown in Table 3.2. The results of our calculations for the various exchange interactions are summarized in the last two columns of Table A.1. We gather from Table A.1, that the dominant exchange interactions are $J_2$ and $J_5$ which are antiferromagnetic. The exchange interactions $J_1$ and $J_6$ are weakly ferromagnetic. It is interesting to note that the estimate of $J_2$ and $J_5$ using the second order perturbation expression is $-11.15 \text{ meV}$ and
3. Electronic structure and magnetic properties in spin gap material: $Sr_2Cu(BO_3)_2$

Figure 3.9: The spin lattice of $Sr_2Cu(BO_3)_2$ is illustrated here.

$-1.42 \text{ meV}$ respectively for $U_{\text{eff}} = 4.5 \text{ eV}$ in good agreement with the exchange interactions obtained from the total energy calculations.

Table A.1 reveals that the only relevant exchange interactions are the intra-dimer coupling $J_2$, and the inter-dimer exchange $J_5$. In contrast to our \textit{ab initio} estimate, $J_5$ corresponding to hopping path $t_3$ and $J_4$ were anticipated to be the dominant inter-dimer exchange interactions based on structural considerations.\(^7\) This in turn suggests that the identification of the exchange paths based on structural consideration may be deceptive and emphasizes the importance of \textit{ab initio} calculations in identifying the dominant exchange paths.

The resulting spin model for $Sr_2Cu(BO_3)_2$ therefore turns out to be a system of coupled dimers as indicated in Fig. 3.9. The figure clearly reveals that the spin lattice is a system of decoupled spin ladders running along crystallographic $b$ axis. The effective spin $1/2$ Heisenberg model for 2 leg ladder ($N \times 2$ lattice) may be written as
3. Electronic structure and magnetic properties in spin gap material: \( \text{Sr}_2\text{Cu(BO}_3)_2 \)

\[ H = \sum_{i=1}^{N} J_2 \vec{S}_{i,1} \cdot \vec{S}_{i,2} + \sum_{i=1}^{N} \sum_{j=1,2} J_3 \vec{S}_{i,j} \cdot \vec{S}_{i+1,j} \]  

(3.2)

3.2.2 Susceptibility and Magnetization

In order to check how the proposed spin model works, we have calculated the magnetic susceptibility as a function of temperature and magnetization both as a function of temperature and field and compared our results with the available experimental data.\(^{(7)}\) We have used the stochastic series expansion (SSE) method to study the finite temperature properties of the Heisenberg antiferromagnet. The SSE is a finite-temperature QMC technique based on importance sampling of the diagonal matrix elements of the density matrix \( \exp(-\beta H) \).\(^{(13-15)}\) The susceptibility calculated by SSE method is:

\[ \chi_{\text{th}} = \beta \langle \langle M^2 \rangle - \langle M \rangle^2 \rangle, \quad \text{with} \quad M = \sum_i S_i^z \]  

(3.3)

\[ \chi = \frac{N_A g^2 \mu_B^2 \chi_{\text{th}}}{k_B J_2} \]  

(3.4)

where, \( N_A \) is the Avogadro number. The QMC simulation of the spin Hamiltonian was carried out by considering finite lattice of \( 96 \times 2 \) sites with periodic boundary conditions, using the stochastic series expansion algorithm.\(^{(13-15)}\) We have used 50,000 steps for thermalization and 5,000,000 steps after thermalization to ensure low statistical errors. To simulate the low-temperature region of the susceptibility data, we have also included the Curie contribution from impurities as \( \chi_{\text{CW}} = C_{\text{imp}} / T \), where \( C_{\text{imp}} = 0.00093 \) emu K/mol Oe. The best fit susceptibility for the dimer model \( (J_2 = 106.66 \text{ K}, \ g = 2.13) \) and the coupled dimer model \( (J_2 = 106.66 \text{ K}, \ \alpha = 0.125 \text{ and } g = 2.146) \) and a comparison with experimental susceptibility is shown in Fig. 3.10. While the overall agreement of the dimer model as well as the coupled dimer model
3. Electronic structure and magnetic properties in spin gap material: Sr$_2$Cu(BO$_3$)$_2$

Figure 3.10: The variation of calculated magnetic susceptibility as a function of temperature is plotted here.

with the experimental data is good but at the low temperature region (see inset of Fig. 3.10) the calculated susceptibility with the coupled dimer model has a better agreement with the experimental data. Also $g = 2.146$ value for the coupled dimer model, is in agreement with the average $g$ value obtained from the electron spin resonance (ESR) experiment.\(^{(7)}\)

Next, we have done the simulation of the quantum spin models with an external magnetic field. The importance of inter-dimer coupling is particularly visible in the magnetization versus field and magnetization versus temperature, shown in Fig. 3.11(a) and Fig. 3.11(b) respectively. Fig. 3.11(a) displays magnetization as a function of field at a very low temperature 1.5 K. We find that our simulation with the coupled dimer model where $J_2 = 106.66$ K, $\alpha = .125$, and $g = 2.146$ is in excellent agreement with the experimental results. We clearly see the upturn in the magnetization occurs at a low magnetic field than that predicted for a dimer model $(H_c = J_2/g\mu_B = 74.6$ T for $J_2 = 106.66$ K and $g = 2.13$). The characteristic cusp like singularity expected for one dimensional (1D) systems and spin ladders\(^{(30,31)}\) is clearly seen in our simulation (see inset of Fig. 3.11(a)). This feature is however absent in the experimental data.
3. Electronic structure and magnetic properties in spin gap material: \( \text{Sr}_2\text{Cu(BO)}_3\text{)}_2 \)

Figure 3.11: Magnetization plotted (a) as a function of applied magnetic field at temperature \( T = 1.5 \text{ K} \) and (b) as a function of temperature in an applied magnetic field strength \( H = 60 \text{ T} \) for dimer model (dotted line) and coupled dimer model (solid line) of \( \text{Sr}_2\text{Cu(BO)}_3\text{)}_2 \). The symbols indicate the experimental data.

possibly due to anisotropies. The simulation using the isolated dimer model \( J_2 = 106.66 \) and \( g = 2.13 \) hardly agrees with the experimental data except for the low field region. Fig. 3.11(b) displays the magnetization as a function of temperature for \( H = 60T < J_2/g \mu_B \) (74.6 T). In the same figure we have shown the results obtained from the isolated dimer model and the experimental data. We again find excellent agreement of the result obtained from the coupled dimer model with the experiment. The figure reveals that the magnetization does not fall to zero at low temperature. At higher temperature the \( M(T) \) curve rise sharply and coincides with the isolated dimer model. These calculations indicate the reliability of our spin Hamiltonian derived from first principles electronic structure calculation.
3.3 Conclusions

We have employed ab initio density functional calculation using TB-LMTO and NMTO down-folding method to study the electronic structure of Sr$_2$Cu(BO$_3$)$_2$. Calculating various effective hopping integrals we find that the intra-dimer exchange interaction is dominant and is responsible for the spin gap seen in the system. In contrast to the structural considerations, our ab initio calculations reveal that the inter-dimer interaction is along the crystallographic $b$ direction and is mediated by super super exchange due to short O-O distances in the exchange pathway. We have derived the relevant spin model for Sr$_2$Cu(BO$_3$)$_2$ and the spin model is a system of decoupled spin ladders (with strong rung coupling) running along the crystallographic $b$ direction.

To check the validity of our proposed spin model we have computed magnetic susceptibility as a function of temperature and magnetization as a function of temperature as well as magnetic field and compared our results with available experimental results. At low temperature and high magnetic field our simulations with the coupled dimer model show excellent agreement with the experimental data. Our calculations support that the coupled dimer model is the appropriate model to describe the physics of Sr$_2$Cu(BO$_3$)$_2$.

Bibliography


3. Electronic structure and magnetic properties in spin gap material: $Sr_2Cu(BO_3)_2$


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3. Electronic structure and magnetic properties in spin gap material: \( \text{Sr}_2\text{Cu(BO)}_3 \)


