SrCu$_2$(BO$_3$)$_2$ under pressure: a first-principle study

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Using density-functional theory (DFT) band-structure calculations, we study the crystal structure, the lattice dynamics, and the magnetic interactions in the Shastry-Sutherland magnet SrCu$_2$(BO$_3$)$_2$ under pressure, concentrating on experimentally relevant pressures up to 4 GPa. We first check that a ferromagnetic spin alignment shortens the nearest-neighbor Cu-Cu distance and reduces the Cu-O-Cu angle compared to the state with the antiferromagnetic spin alignment in the dimers, in qualitative agreement with the structural changes observed at ambient pressure as a function of temperature and applied field. Next, we determine the optimal crystal structures corresponding to the magnetic structures respectively consistent with the dimer phase realized at ambient pressure, the Néel ordered phase realized at high pressures, and two candidates for the intermediate phase with two types of dimers and different stackings. For each phase, we performed a systematic study as a function of pressure, and we determined the exchange interactions and the frequencies of several experimentally relevant phonon modes. In the dimer phase, the ratio of the inter- to intra-dimer couplings is found to increase with pressure, in qualitative agreement with recent experiments. In the Néel phase, the frequency of the pantograph mode is larger than the extrapolated value from the dimer phase, again in agreement with the experimental results, and accordingly the intradimer coupling is smaller than the extrapolated value from the dimer phase. Finally, all tendencies inside the candidate intermediate phases are thoroughly worked out, including specific predictions for some Raman active phonon modes that could be used to pin down the nature of the intermediate phase.

I. INTRODUCTION

After being one of the main players in the field of frustration-induced magnetization plateaus, strontium copper borate SrCu$_2$(BO$_3$)$_2$ is now systematically studied under pressure. This compound consists of well separated layers of [CuBO$_3$]$^-$ structural elements stacked along the $c$ axis. Each magnetic Cu$^{2+}$ ion carries a spin $S = 1/2$, leading to a 2D arrangement of mutually orthogonal dimers (Fig. 1), a model topologically equivalent to the Shastry-Sutherland (SS) model (see Fig. 2) defined by the Hamiltonian:

$$\hat{H} = J \sum_{\langle i,j \rangle} \hat{S}_i \cdot \hat{S}_j + J' \sum_{\langle\langle i,j \rangle\rangle} \hat{S}_i \cdot \hat{S}_j$$  \hspace{1cm} (1)

The Cu$^{2+}$ spins of a dimer are coupled by an intra-dimer exchange integral $J$ involving a Cu – O – Cu path, while the spins of the neighboring dimers interact through an inter-dimer coupling $J'$. In the limit $\alpha = J'/J \rightarrow 0$, the ground state is an exact product of dimer singlets and the spectrum is gapped, while in the $\alpha \rightarrow \infty$ limit, the model reduces to the standard Heisenberg model on the square lattice, with long-range antiferromagnetic order and a gapless spectrum. In between, after some debate, it is now well accepted, based on numerical evidence, that there in an intermediate plaquette phase in the range $\alpha = 0.675 \div 0.76$. In this phase, strong bonds form around empty plaquettes, leading to a two-fold degenerate ground state with broken translational symmetry and a gapped spectrum. Various experiments have shown that, at ambient pressure, the parameter $\alpha$ is around 0.63 in SrCu$_2$(BO$_3$)$_2$, putting the system in the dimer phase, but not too far from the intermediate plaquette phase. This has been confirmed by ab-initio calculations done for the ambient-pressure crystal structure.

To explore this phase diagram experimentally, it has been proposed early on to use pressure to increase the ratio $\alpha$, and indeed a phase transition around 2 GPa has been detected first by NMR and then confirmed by inelastic neutron scattering (INS), magnetization measurements, electron spin resonance (ESR) and thermodynamic measurements. However, the properties of this phase do not seem to be consistent with the plaquette phase predicted by the numerical results obtained on the Shastry-Sutherland model. In particular, NMR reveals the presence of two different Cu sites in an applied field, whereas in the plaquette phase of the Shastry-Sutherland model all magnetic sites remain equivalent. Even in zero field there seems to be a problem with the plaquette phase. Indeed, the structure factor revealed by neutron scattering seems to be more consistent with another plaquette phase in which strong bonds form around plaquettes with diagonal couplings, a phase naturally leading to two types of Cu sites.

On the theory side, it has been shown that this
phase with two different copper sites can be stabilized by a distortion that would lead to two types of inter-and intra-dimer couplings, and to be essentially one-dimensional. Accordingly, it has been called the Haldane or full plaquette phase (FFP) (Fig. 10), by contrast to the empty plaquette phase (EPP) of the Shastry-Sutherland model (Fig. 2).

To make progress on the properties of SrCu$_2$(BO$_3$)$_2$ under pressure, and in particular on the identification of the intermediate phase, it is of utmost importance to have more precise information on the structure of the system, and on the exchange couplings that describe its magnetic properties, as a function of pressure. The goal of the present paper is to address this issue with ab-initio calculations, the only ab-initio calculations available so far being, to the best of our knowledge, limited to ambient pressure.

**II. COMPUTATIONAL METHODS AND MODELS**

*Electronic structure calculations.* Density-functional band-structure calculations for SrCu$_2$(BO$_3$)$_2$ were performed within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional as implemented in the Vienna *ab initio* simulation package VASP with the plane-wave basis set. In these calculations, we set the energy cutoff to 920 eV and the energy convergence criteria to $10^{-7}$ eV. For the Brillouin zone integration a $4 \times 4 \times 4$ Monkhorst-Pack mesh was used. In order to check the possible convergence errors and structural relaxation error arising due to the incompleteness of the basis set known as Pulay stress, all calculations were compared with those obtained using a 1100 eV energy cutoff and a $6 \times 6 \times 6$ k-mesh. Correlation effects were taken into account within the static mean-field DFT+U approach with fully localized limit (FLL) for the double counting correction.

*Structural optimization.* The crystal structure of SrCu$_2$(BO$_3$)$_2$ at low temperature and ambient pressure was taken from Ref. 24. In accordance with experimental studies, we consider pressures ranging from 0 to 4 GPa. Both the lattice parameters and the atomic positions were allowed to relax under fixed hydrostatic pressure until all the residual force components of each atom were less than $5 \times 10^{-4}$ eV/Å. The convergence in interatomic distances, exchange interactions, and phonon frequencies is $10^{-4}$Å, 1 K, and 0.1 cm$^{-1}$, respectively. All these parameters may deviate from the experimental values due to systematic errors in DFT, but their relative changes between the different magnetic configurations or as a function of pressure are significant and robust, as we show below.

The symmetry of the optimized structures was analyzed by the FINDSYM software. We used the finite displacement method for the calculation of phonon spectra at the $\Gamma$ point and the SAM application on the Bilbao Crystallographic Server to analyse the symmetry of the calculated modes.

*Magnetic model.* The exchange interaction parameters $J$ and $J'$ of the spin Hamiltonian, Eq. 1, were extracted.
from the total energy of ordered collinear spin configurations using the mapping procedure, within the DFT+U method which, in the simplest case of two spins, can be written as

\[ J = (E_{FM} - E_{AFM})/2S^2, \]  

(2)

where \( E_{FM} \) and \( E_{AFM} \) denote the energy of the system in the ferromagnetic and antiferromagnetic configurations respectively.

**Electronic model.** In order to give a microscopic explanation of the obtained interatomic exchange interactions, we perform a parametrization of the DFT band spectra of SrCu\(_2\)(BO\(_3\))\(_2\) around the Fermi level by constructing maximally localized Wannier functions, as implemented in the wannier90 package. More specifically, we construct the following tight-binding model:

\[ \hat{H}_{TB} = \sum_{ij,\sigma} t_{ij} \epsilon^{\sigma}_{ij} c_{ij,\sigma}^\dagger c_{ij,\sigma}, \]

(3)

where \( t_{ij} \) is the hopping integral between the \( i \)th and \( j \)th Wannier functions. On the basis of these Wannier functions, one can perform a microscopic analysis of the exchange interactions by using a superexchange theory approach.

\[ J_{ij} = J_{ij}^{\text{kin}} + 2J_{ij}^{F} = \frac{4t_{ij}^2}{U_{ij}} + 2J_{ij}^{F}. \]

(4)

Here \( U_{ij} = U_{ii} - U_{ij} \) is an effective screened Coulomb parameter. The first term has a superexchange origin, whereas the second term, the so-called non-local exchange interaction, arises due to the direct overlap of the wave functions. All these parameters can be estimated by using the parametrization of the electronic structure obtained with first-principles calculations, which will be discussed below.

**Adjusting the DFT+U parameters.** SrCu\(_2\)(BO\(_3\))\(_2\), as well as other Cu\(^{2+}\) oxide materials, with partially occupied 3\(d\) energy bands, belongs to the family of correlated insulators. Its ground-state properties, including magnetic moments and energy band gap, should be described by taking into account Coulomb correlations in the 3\(d\) states of copper atoms. In our case, we use the DFT+U method. Such an approach requires the choice of the on-site Coulomb \( U \) value, which can be different for different transitional-metal oxides. It is a common practice to consider \( U \) as an empirical parameter, and to adjust it to better fit experimental data. Consequently, the results of the structural optimization will depend not only on the specific magnetic order under consideration, but also on the value of \( U \). In this work, we fix \( U \) first and then determine the optimized crystal structures for different types of magnetic order.

In our study, we performed calculations with several values of \( U \), as shown in Fig. 3. As one could expect, increasing \( U \) amplifies the localization of the Cu 3\(d\) electrons, as revealed by analyzing the magnetic moments of the copper and oxygen atoms. The choice of the \( U \) value also affects the resulting exchange interactions and corresponding structural properties. We emphasize that after comparing the exchange interactions calculated for different \( U \) with available experimental estimates, we choose \( U = 11.2 \) eV as the value that gives the best agreement between experimental and theoretical exchange couplings at ambient pressure. This value will be used to describe the magnetic behavior of SrCu\(_2\)(BO\(_3\))\(_2\) under pressure. Note that a similar value of the on-site Coulomb \( U \) was previously used to study another copper oxide system, for which a reasonable agreement between calculated thermodynamics quantities, such as magnetization and magnetic susceptibility, and experimental data was reported.

The intra-atomic exchange interaction \( J_{HH} \), another important parameter of the DFT+U scheme, was fixed at 1 eV. This value is chosen in a semi-empirical manner on the basis of previous works on Cu\(^{2+}\) oxide materials, in which the DFT+U results agree with available experimental data.
III. TETRAGONAL STRUCTURES

The main focus of our study is on the magnetic properties of SrCu$_2$(BO$_3$)$_2$, considering first a description in terms of the Shastry-Sutherland model. The ground state of SrCu$_2$(BO$_3$)$_2$ at ambient pressure is a product of dimer singlets. This is a many-body magnetic state that cannot be reproduced within a one-particle numerical approach such as the GGA approximation of the density functional theory we used. A standard practice in this situation is to define a one-particle magnetic state characterized by an antiferromagnetic configuration of the spins belonging to the dimer. We will further refer to such a configuration as Dimer. We also consider other types of magnetic configurations, for instance the ferromagnetic (FM) alignment of the copper spins (Fig. 4) that can be thought as a mean-field representation of the many-body singlet state induced by an external magnetic field. Additionally, we consider Néel magnetic order, which is the only long-range order state realized in the Shastry-Sutherland model used in this work to simulate the many-body magnetic states at ambient pressure first. According to the experimental data, at ambient pressure the intradimer Cu – Cu distance $d$ and the Cu – O – Cu angle $\gamma$ change in the temperature range where spin-spin correlations set in. Below $40\,K$, both $d$ and $\gamma$, as well as the lattice parameter $a$ increase ($\frac{\Delta a}{a}|_{T=40\,K} = 1.7 \times 10^{-4}$). At the same time, in high magnetic fields the lattice parameter $a$ becomes smaller ($\frac{\Delta a}{a}|_{H=50\,T} = -1.4 \times 10^{-4}$), which can lead to a reduction in $d$ and $\gamma$. It means that the formation of the triplet state shrinks the dimer, whereas the formation of the singlet state expands it. This effect can be explained by a significant spin-lattice coupling. Since we simulate the many-body singlet and triplet states with one-particle Dimer and ferromagnetic configurations at the DFT level, it is interesting to compare the optimized structural parameters and exchange couplings for these two distinct magnetic orders.

At ambient pressure, the difference in the intradimer Cu – Cu distance $d$ between the Dimer and FM configurations is $\Delta d = d_{\text{Dimer}} - d_{\text{FM}} \approx 0.006\,\text{Å}$, while the difference in the Cu – O – Cu angle $\Delta \gamma \approx 0.28^\circ$, which are in reasonable agreement with previous ab-initio results obtained using another DFT code ($\Delta d = 0.009\,\text{Å}$ and $\Delta \gamma = 0.43^\circ$).

The experimental estimates allow us to perform a similar analysis between the low-temperature singlet and high-temperature paramagnetic states. $\Delta d = d_{T=2K} - d_{T=40\,K} \approx 0.013\,\text{Å}$, and $\Delta \gamma = \gamma_{T=2K} - \gamma_{T=40\,K} \approx 0.5^\circ$. Comparing $\Delta d$ and $\Delta \gamma$ we conclude that the theoretical parameters are in a reasonable range.

On the basis of the optimized unit cell, we have further calculated the corresponding values of the $J$ and $J'$ exchange couplings. As one can expect from the structural information, the Dimer order demonstrates a stronger intradimer $J$ coupling, in agreement with the Goodenough-Kanamori rule: $J_{\text{FM}} = 75.6\,\text{K}$, $J_{\text{Dimer}} = 83.8\,\text{K}$, the ratio $J_{\text{FM}}/J_{\text{Dimer}} = 0.90$. On the other hand, the interdimer $J'$ couplings are almost the same for each magnetic configuration, $J'_{\text{FM}} = J'_{\text{Dimer}} = 41.7\,\text{K}$. It means that the type of magnetic order has no sig-
significant influence on the interdimer magnetic interaction. These findings are in qualitative agreement with the previous ambient-pressure study that showed a reduction of approximately 10% in the $J$ value, but no detectable changes of the interdimer coupling $J'$ for different types of magnetic order. However, the values of the exchange couplings reported in the present paper are in much better agreement with the experiment.

### B. Pressure evolution

In this section, we discuss the results of the structural optimization of SrCu$_2$(BO$_3$)$_2$ as a function of external pressure and magnetic order. All structural parameters reduce as pressure increases, which leads to a modification of the exchange couplings as will be discussed below. The optimized structural parameters under pressure are listed in Table I for the Dimer and Néel configurations, which are the relevant configurations in zero external field at lower and higher pressures, respectively. Since the spins on the dimers are parallel in both the ferromagnetic and Néel configurations, the structural parameters and ensuing magnetic interactions have similar values therein.

| $P$ (GPa) | Dimer | Néel | Dimer | Néel |
|-----------|-------|------|-------|------|
| 0[^1]     | 2.931 | -    | 98.478| -    |
| 1[^24]    | 2.922 | -    | 97.851| -    |
| 2         | 2.897 | 2.891| 97.470| 97.186|
| 3         | 2.889 | 2.883| 97.346| 97.068|
| 3.3[^24]  | 2.882 | 2.875| 97.257| 96.983|
| 4         | 2.875 | 2.868| 97.194| 96.926|

The exchange interactions as a function of pressure, $J(P)$ presented in Fig. 5, have the same slope in the case of Dimer and Néel orderings. By extrapolating the data to higher and lower pressures, respectively, we detect a finite shift between the corresponding $J$ values, which stems from the aforementioned spin-lattice coupling. One possible scenario is that $J(P)$ changes abruptly in the intermediate region. It is supported by the recent theoretical results reported in Ref. [5]. More specifically, the spin-spin correlation function $\langle S_i^z S_j^z \rangle$ for the shortest-distance copper pair coupled by the $J$ exchange interaction has a discontinuity at $\alpha_d = 0.675$, the transition point to the intermediate phase[^6]. Due to the interplay between spin and lattice degrees of freedom, such a discontinuity of the $\langle S_i^z S_j^z \rangle$ function can be expected to modify the equilibrium intradimer distance $d$ and the Cu – O – Cu angle $\gamma$, which will result in an abrupt variation of $J(P)$. The experimental estimates of the exchange interactions taken from Ref. [11] and [13] do not cover the intermediate phase, thus this is just a prediction at that stage.

At lower pressures, in the dimer phase, our ab-initio estimates of the exchange interactions are in better agreement with recent ESR results[^13] than with those extracted from thermodynamic measurements[^11]. The slope of the pressure dependence is well reproduced, whereas deviations in the absolute values can be ascribed to a systematic error within DFT. This error affects our computational estimate of $\alpha$ that comes out lower than 0.675 required for the breakdown of the singlet phase of the Shastry-Sutherland model.

To demonstrate the systematic nature of this error, we first note that the intradimer coupling $J$ is a short-range coupling consisting of a ferromagnetic direct exchange and antiferromagnetic superexchange, see Eq. (4). The former involves a significant error bar when calculated by DFT[^23], but its microscopic origin is well known and for cuprates it comes from the Hund’s coupling on the ligand site[^27]. The size of $J^F$ depends on the contribution of the

![Figure 5](image-url)

**FIG. 5.** Pressure evolution of the interdimer $J$ and intradimer $J'$ isotropic exchange interactions and their ratio $\alpha = J'/J$. The interactions were estimated for the structures obtained with Néel and Dimer magnetic configurations. The phase boundaries are taken from Ref. [14]. For comparison, we provide the available experimental estimates obtained from thermodynamic measurements (TM, green dots) and electron spin resonance (ESR, orange dots) data. Green and orange lines represent interpolation of the experimental data.
ligand orbitals to the Cu $d_{x^2-y^2}$ Wannier function. In our case, this contribution (and, therefore, $J_F$ itself) is nearly independent of pressure, as can be seen from the spread of the Wannier functions (Table II) that decreases only slightly following the lattice compression.

All pressure-induced changes in $J$ are thus related to the antiferromagnetic contribution $J_{kin}$ that depends on the hopping parameter $t$ and, consequently, on the Cu–O–Cu angle $\gamma$ according to $t \sim \cos \gamma$. The $\gamma$ value is systematically reduced under pressure, which decreases $J$, increases $\alpha$, and drives SrCu$_2$(BO$_3$)$_2$ through its pressure-induced magnetic transitions. DFT captures this trend very well, as can be seen from the perfect match between the slope of $J(P)$ obtained in our work and measured experimentally by ESR.

**TABLE II.** Spreads of Wannier functions of $x^2-y^2$ symmetry, calculated at different values of the external pressure and with different magnetic ordering (in Å$^2$).

|         | 0 GPa | 1 GPa | 2 GPa | 3 GPa | 4 GPa |
|---------|-------|-------|-------|-------|-------|
| Néel    | 2.648 | 2.640 | 2.631 | 2.621 | 2.611 |
| Dimer   | 2.695 | 2.687 | 2.679 | 2.668 | 2.658 |

**FIG. 7.** (Left) Pressure evolution of the interdimer $t$ and intradimer $t'$ hopping parameters calculated in the basis of Wannier functions. (Right) Exchange couplings, obtained within Eq. 4, compared to the ESR data (orange dots and line).

**C. Pantograph mode simulations**

Previous experimental studies suggested a strong spin-lattice coupling in SrCu$_2$(BO$_3$)$_2$. This motivates the modeling of phonon spectra using different magnetic configurations, as well as crystal structures optimized under pressure.

**FIG. 8.** Pantograph mode atomic displacements according to DFT+$U$ simulations. The sizes of the arrows are proportional to the displacement vectors obtained from the calculations. See Fig. 1 for more information about the crystal structure of SrCu$_2$(BO$_3$)$_2$.

Our focus is on the so-called pantograph mode, schematically represented in Fig. 8. It directly modulates the dimer bond length $d$ and the Cu–O–Cu angle $\gamma$, thus modifying the intradimer coupling $J_8$. Recently, using Raman scattering it was shown that this...
mode exhibits a very strong pressure and temperature dependence.\textsuperscript{15} The relative frequency shift of the pantograph mode between 40 K and 2.6 K shows an abrupt change at $P_1 \sim 1.5$ GPa and gradually increases, switching sign at about $P_2 \sim 2.2$ GPa. Since the pantograph mode is related to the intradimer geometry, the observed pressure dependence can be related to the dimer bond energy $J \langle S_1 \cdot S_2 \rangle$. Thus, the estimated critical pressure values can be expected to reflect the transitions from dimer singlet to the intermediate state at $P_1$ and from intermediate phase to Néel at $P_2$ reported in recent high-pressure thermodynamic measurements.\textsuperscript{15}

\textbf{IV. INTERMEDIATE MAGNETIC PHASE}

\textbf{A. Haldane-type candidate}

The realization of the intermediate empty plaquette phase (Fig. 2) implies that the system preserves its tetragonal symmetry under pressure. However, this is not the only possibility. The magnetic lattice of SrCu$_2$(BO$_3$)$_2$ is highly frustrated, and the frustration degree is controlled by the ratio $\alpha = J'/J$: The degree of frustration is higher in the intermediate phase between the unfrustrated limits of decoupled singlets and square-lattice antiferromagnet. In order to release such a frustration, the system may experience some distortions of the tetragonal crystal structure under pressure. This can be studied with DFT to complete existing experimental data.

One of the possible distortion scenario has been proposed by Boos et al.\textsuperscript{17} The authors have studied an extended Shastry-Sutherland model with nonequivalent intradimer $J_1$, $J_2$ and interdimer $J'_1$, $J'_2$ couplings. It was found that if $J_1$ and $J_2$ are sufficiently different, it is possible to stabilize the so-called full plaquette (FPP) phase. By contrast to the empty plaquette phase (EPP), which is known to be realized in the intermediate phase of the Shastry-Sutherland model (Fig. 2), the FPP is characterized by stronger correlations around plaquettes with diagonal couplings, effectively forming chains in the two-dimensional magnetic lattice (Fig. 10), and it is adiabatically connected to the Haldane magnetic phase suggested in Ref. 16. The calculated structure factor agrees with neutron scattering experimental data under pressure.\textsuperscript{17} Moreover, numerical studies demonstrate that the spin gap $\Delta$ increases as $\alpha$ increases in the case of the EPP, while the corresponding Haldane magnetic phase demonstrates a reduction of $\Delta$ in agreement with recent specific heat measurements under pressure.\textsuperscript{17}

Thus the next important step of our investigation is to choose the best representation of the FPP/Haldane magnetic phase of SrCu$_2$(BO$_3$)$_2$ in terms of a one-particle magnetic configuration to be studied within mean-field DFT. To that end, we will consider a magnetic order that is characterized by ferromagnetic dimers in one crystallographic direction and antiferromagnetic dimers in the orthogonal in-plane direction (Fig. 10). In this way, FM dimers will behave as effective magnetic sites with spin $S = 1$ interacting through AFM bonds. As shown in Sec. III FM and AFM ordered dimers have different Cu – Cu distances $d$ and Cu – O – Cu angles $\gamma$. Thus, it is expected that such a magnetic order will break the initial tetragonal symmetry.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig9.png}
\caption{Pressure evolution of the pantograph mode frequency: comparison of the phonon mode for Dimer and Néel ordered magnetic lattices from DFT $+U$ simulations with experimental data measured at 2.6 K.\textsuperscript{14} The phase boundaries are taken from Ref. 14. The violet line is just a schematic plausible interpolation of the phonon mode inside the intermediate magnetic phase.}
\end{figure}
FIG. 10. (Top) Haldane magnetic state and its representation with the magnetic configuration used in this work. (Bottom) Crystal structure of SrCu$_2$(BO$_3$)$_2$, where in Haldane (a) AFM ordered dimers are oriented in the same direction for both structural layers, and in Haldane (b) this direction alternates from one layer to the next.

In the case of the three-dimensional magnetic structure, there are two possibilities for the magnetic order within the unit cell: AFM ordered dimers are oriented in the same direction or alternate from one layer to the next. Depending on this, the crystal structure will be modified accordingly.

**B. Structural properties**

Let us consider the situation where all AFM ordered dimers are parallel to the $a + b$ direction in both layers of the unit cell. In Fig. 10, such an order is labeled as Haldane (a).

|TABLE III. Optimized structural parameters of SrCu$_2$(BO$_3$)$_2$ with Haldane (a) magnetic order (Fig. 10).|
|---|
|P (GPa) | $d_{1}^{AFM}$ (Å) | $d_{2}^{AFM}$ (Å) | $\gamma_{1}^{AFM}$ (deg) | $\gamma_{2}^{AFM}$ (deg) |
|---|---|---|---|---|
|0 | 2.896 | 2.891 | 97.439 | 97.215 |
|1 | 2.889 | 2.883 | 97.317 | 97.096 |
|2 | 2.882 | 2.876 | 97.233 | 97.008 |
|3 | 2.875 | 2.869 | 97.172 | 96.953 |
|4 | 2.868 | 2.862 | 97.120 | 96.904 |

The magnetic structure considered above is only one of the possible representations consistent with a many-body Haldane phase in each layer. Another possibility is that the AFM dimers alternate in the crystal structure. Such a configuration is denoted as Haldane (b) in Fig. 10. In this case, the $ab$ plane distortions are eliminated (Table IV) because the AFM dimers with long $d$ distance are orthogonal between neighbouring layers, leading to a compensation of the elongation of the unit cell in one specific direction. This alternation results in twice smaller differences $\Delta d \sim 0.003$ Å, and $\Delta \gamma \sim 0.14^\circ$. In this case, the system is characterized by the $P2_1$ space group (No. 3), i.e. the symmetry is lower than in the Haldane (a) phase.

|TABLE IV. Structural parameters of SrCu$_2$(BO$_3$)$_2$ optimized at different values of external pressure. These results were obtained with the Haldane (b) magnetic order (Fig. 10).|
|---|
|P (GPa) | $d_{1}^{AFM}$ (Å) | $d_{2}^{AFM}$ (Å) | $\gamma_{1}^{AFM}$ (deg) | $\gamma_{2}^{AFM}$ (deg) |
|---|---|---|---|---|
|0 | 2.895 | 2.892 | 97.398 | 97.255 |
|1 | 2.888 | 2.885 | 97.276 | 97.134 |
|2 | 2.881 | 2.878 | 97.190 | 97.049 |
|3 | 2.873 | 2.870 | 97.132 | 96.993 |
|4 | 2.867 | 2.864 | 97.084 | 96.945 |

The magnetic structure considered above is only one of the possible representations consistent with a many-body Haldane phase in each layer. Another possibility is that the AFM dimers alternate in the crystal structure. Such a configuration is denoted as Haldane (b) in Fig. 10. In this case, the $ab$ plane distortions are eliminated (Table VI) because the AFM dimers with long $d$ distance are orthogonal between neighbouring layers, leading to a compensation of the elongation of the unit cell in one specific direction. This alternation results in twice smaller differences $\Delta d \sim 0.003$ Å, and $\Delta \gamma \sim 0.14^\circ$. In this case, the system is characterized by the $P2_1$ space group (No. 3), i.e. the symmetry is lower than in the Haldane (a) phase.

**C. Exchange interactions**

The calculated values of the exchange interactions are given in Fig. 11. It is interesting to note that the magnetic configurations representing the Haldane phases lead to rather different values of $J_1$ and $J_2$. In the Haldane (a) phase, the smallest value of $J_1$ is outside the window obtained by extrapolating the values of $J(P)$ in the Dimer and in the Néel phases, while in the Haldane (b) phase, both $J_1$ and $J_2$ are inside that window.

The magnetic configurations representing the Haldane phases should also affect the interdimer couplings $J'$. Indeed, in the $J_2 > J_1$ case, the relation $J'_2 < J'_1$ should hold because the increase in $J$ through the increasing Cu – O – Cu angle $\gamma$ will lead to a decrease in the Cu – O – O – Cu angle, which may eventually reduce $J'$. However,
Resonance is also sensitive to structural distortions, but so far this method did not reveal any distortion in the intermediate phase.

Alternatively, structural distortions can be detected by Raman scattering under pressure. In particular, the symmetry analysis of the undistorted tetragonal structure with the space group $I\overline{4}2m$ gives the following representation of the optical modes:

$$\Gamma_{\text{optic}} = 9A_1 + 7A_2 + 6B_1 + 9B_2 + 16E. \quad (5)$$

All the modes except $A_2$ are Raman active, while only $B_2$ and $E$ are infra-red (IR) active. According to the selection rules for Raman scattering, only modes with specific symmetry can be observed for a given polarization. Structural distortions may lead to violation of such selection rules, implying that modes become observable in several polarizations, which would not be possible in the tetragonal phase.

In particular, the pantograph mode analyzed in Sec. III C has $A_1$ symmetry in the tetragonal phase. It can be observed in the $\tau(aa)c$ polarization, but remains silent in the $\tau(ab)c$ polarization. The magnetic configurations (a) and (b) of Haldane type modify the symmetry of this mode to $A'$ and $A$, respectively, activating it for both $\tau(aa)c$ and $\tau(ab)c$ polarizations. Thus, this mode will not allow to determine the type of distortion (Haldane (a) or (b)), but it could give direct evidence that the distortion occurs if such a selection rule violation takes place (Fig. 12). Thus, it would be highly desirable to look for violations of the selection rules in Raman scattering experiments under pressure.

V. CONCLUSIONS

In this work, we studied the structural and magnetic properties of SrCu$_2$(BO$_3$)$_2$ under pressure by using density-functional-theory methods. Depending on the pressure value, different one-particle magnetic configurations approximating quantum magnetic states were considered: i) Dimer for the singlet state at low pressures, in which nearest-neighbor copper pairs are exact singlets; ii) ferromagnetic for the fully polarized state that would be realized in a high magnetic fields; iii) Néel for the high-pressure phase in which the intradimer correlations are ferromagnetic (as the diagonal correlations in the Néel state on the square lattice); and iv) magnetic configurations of Haldane type in the intermediate pressure phase in which half of the nearest-neighbor dimers have antiparallel spins and the remaining half have parallel spins. In all cases, we observed that the choice of a particular magnetic order modifies the crystal structure. For instance, ferromagnetically ordered SrCu$_2$(BO$_3$)$_2$ would be characterized by a shorter intradimer distance than in the case of the Dimer configuration. More importantly, the obtained pressure dependence of the ratio $\alpha = J'/J$ is in qualitative agreement with the available experimental data.
FIG. 12. Pressure evolution of the pantograph mode frequencies: comparison of the experimental data measured at 2.6 K and theoretical values of the phonon mode calculated with Dimer and Néel magnetic configurations. The dashed line represents the phase boundaries from Ref. 14. The frequencies within the Haldane phases are given for comparison.

We have determined the possible structural distortions induced in SrCu$_2$(BO$_3$)$_2$ by magnetic configurations that combine AFM and FM dimers and can be considered as the mean-field analogs of the quantum Haldane magnetic state. The stabilized structures comprise two nonequivalent dimers with different couplings $J_1$ and $J_2$, with the $J_1/J_2$ ratio in the range of the Haldane/FPP magnetic state in the phase diagram of the extended Shastry-Sutherland model. Finally, on the basis of the symmetry analysis of the calculated phonon modes, we discuss possible ways to detect the intermediate magnetic state in Raman scattering experiments.

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**Appendix A: Atomic positions for Haldane magnetic states**

Here we provide the atomic positions, optimized within DFT+$U$ method ($U = 11.2$ eV, $J_H = 1$ eV) without external pressure. The magnetic order during the optimization was fixed as Haldane (a) and (b) (Fig. 10).

### TABLE V. Structural parameters of SrCu$_2$(BO$_3$)$_2$, optimized at ambient pressure with Haldane (a) magnetic order (Fig. 10).

| $a$ | $b$ | $c$ |
|-----|-----|-----|
| 7.2248 Å | 12.7235 Å | 6.8363 Å |
| $\alpha = \gamma = 90^\circ$ | $\beta = 118.236^\circ$ |
| Space group is $Cm$ (No. 7) |

| Atom | $x$ | $y$ | $z$ |
|------|-----|-----|-----|
| Sr1  | 0.5000 | 0.2500 | -0.2500 |
| O1   | -0.8002 | 0.5973 |
| O2   | -0.1998 | 0.3864 |
| O3   | 0.0000 | 0.2063 |
| O4   | -0.5303 | 0.0912 |
| O5   | -0.5303 | 0.0912 |
| O6   | -0.8177 | 0.2652 |
| O7   | -0.1821 | 0.2348 |
| Cu1  | -0.2275 | 0.0998 |
| Cu2  | -0.7725 | 0.4088 |
| Cu3  | 0.0000 | 0.3864 |
| O1   | -0.8002 | 0.5973 |
| O2   | -0.1998 | 0.3864 |
| O3   | 0.0000 | 0.2063 |
| O4   | -0.5303 | 0.0912 |
| O5   | -0.5303 | 0.0912 |
| O6   | -0.8177 | 0.2652 |
| O7   | -0.1821 | 0.2348 |
| Sr1  | -0.5000 | 0.2500 |

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TABLE VI. Structural parameters of SrCu$_2$(BO$_3$)$_2$, optimized at ambient pressure with Haldane (b) magnetic order (Fig. 10).

\[
a = b = 8.9993 \text{ Å}, \quad c = 6.8362 \text{ Å}
\]
\[
\alpha = \beta = \gamma = 90^\circ
\]

Space group is $P_2_1$ (No. 3)

| B1  | 2e  | 0.7063 | 0.2937 | 0.7600 |
|-----|-----|--------|--------|--------|
| B2  | 2e  | 0.2937 | 0.7063 | 0.7599 |
| B3  | 2e  | 0.2063 | 0.7938 | 0.2598 |
| B4  | 2e  | 0.7938 | 0.2063 | 0.2599 |
| Cu1 | 2e  | 0.8862 | 0.1137 | 0.7111 |
| Cu2 | 2e  | 0.1137 | 0.8863 | 0.7111 |
| Cu3 | 2e  | 0.3864 | 0.6136 | 0.2110 |
| Cu4 | 2e  | 0.6136 | 0.3864 | 0.2109 |
| O1  | 2e  | 0.6000 | 0.4000 | 0.7990 |
| O2  | 2e  | 0.4001 | 0.5998 | 0.7990 |
| O3  | 2e  | 0.0998 | -0.0998| 0.2986 |
| O4  | 2e  | -0.0998| 0.0998 | 0.2986 |
| O5  | 2e  | 0.6740 | 0.1437 | 0.7414 |
| O6  | 2e  | 0.3260 | 0.8563 | 0.7414 |
| O7  | 2e  | 0.8563 | 0.6740 | 0.2587 |
| O8  | 2e  | 0.1437 | 0.3260 | 0.2586 |
| O9  | 2e  | 0.1741 | 0.6437 | 0.2415 |
| O10 | 2e  | 0.8260 | 0.3564 | 0.2413 |
| O11 | 2e  | 0.3563 | 0.1740 | 0.7587 |
| O12 | 2e  | 0.6436 | 0.8259 | 0.7585 |
| Sr1 | 1a  | 0      | 0.5000 | 0      |
| Sr2 | 1c  | 1/2    | 0.0000 | 0      |
| Sr3 | 1d  | 1/2    | 0.0000 | 1/2    |
| Sr4 | 1b  | 0      | 0.5000 | 1/2    |

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