Structural distortions in the spin-gap regime of the quantum antiferromagnet \( \text{SrCu}_2(\text{BO}_3)_2 \)

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1. Introduction

Low-dimensional systems with a quantum-disordered singlet ground state have attracted much attention in the past years, both from the experimental as well as from the theoretical point of view. The Haldane \( (S=1, \text{Y}_2\text{BaNiO}_5) \) [1], spin-Peierls \( (S=\frac{1}{2}, \text{CuGeO}_3) \) [2], ladder \( (S=\frac{1}{2}, \text{SrCu}_2 \text{O}_3) \) [3] and plaquette \( (S=\frac{1}{2}, \text{CaV}_4 \text{O}_9) \) [4] systems are members of the broader family, with a spin excitation gap from the nonmagnetic singlet ground state to the first excited triplet state. Quantum spin fluctuations and/or magnetic anisotropy often play a decisive role in the determination of the nature of the ground state properties. A rich variety of phenomena have been observed and predicted in this type of materials; therefore, the discovery of other examples of chemical compounds is worthy as it can promote the understanding of fundamental processes governing the spin-dynamics in the quantum critical regime.

More than twenty years ago, Shastry and Sutherland proposed an interesting theoretical model [5]; they calculated the ground state of an anisotropic quantum spin Heisenberg Hamiltonian with next-neighbor interactions in two dimensions. \( \text{SrCu}_2(\text{BO}_3)_2 \) is a Heisenberg system which displays a unique exchange topology. This compound is indeed one of the first experimental realizations of the two-dimensional (2D) Shastry–Sutherland lattice [6,7], in which a rectangular network of spin-1/2 \( \text{Cu}^{2+} \) dimers is arranged within a square-based structure with diagonal bonds, allowing for nearest- \( (J_1, \text{intra-dimer exchange pathway}) \) and next-nearest- \( (J_2, \text{inter-dimer exchange pathway}) \) neighbor dimer interactions (Fig. 1). \( \text{SrCu}_2(\text{BO}_3)_2 \) presents a dimerized nonmagnetic ground state [8,9], with an energy gap of \( \Delta = 34(1) \text{K} \) [7,10] between the singlet and the triplet states.

As the strong interplay between the crystal structure and the magnetic properties is a well-known aspect of low-dimensional systems, in the recent years many theoretical works were motivated from the phase diagram of the general Shastry–Sutherland lattice type [11]. For the original 2D model, the exact dimer ground state is realized for small \( x = |J_2/J_1| \). Although there are still open questions, there is reasonable consent that when the exchange interactions are tuned to a critical value \( x_c \) of about 0.7,
the attempt to stabilise a long-range ordered antiferromagnetic (AFM) state, however, with no success so far.

The intriguing behaviour in SrCu$_2$(BO$_3$)$_2$ is due to its magnetic anisotropy that appears not well understood up till now. As the crystal structure is anisotropic, with a rather large $J_1$ exchange coupling, the main contribution to spin anisotropy was shown [23] to be of Dzyaloshinsky–Moriya (DM) type, whose presence obeys a number of rules posed by the crystal symmetry. Therefore the knowledge of the low-temperature crystal structure is crucial for the understanding of the magnetic properties of SrCu$_2$(BO$_3$)$_2$. While the crystal structure has been determined quite comprehensively by single crystal X-ray diffraction measurements down to 100 K [24], no structural studies have been pursued up to now at lower temperatures where novel quantum mechanical magnetic behaviour was found [6–10]. Since accurate knowledge of the lattice symmetry is necessary to rationalise the ground state properties, here we report a detailed structural study for SrCu$_2$(BO$_3$)$_2$ at low-temperatures. We performed high-resolution neutron powder diffraction (NPD) measurements between room temperature (RT) and down to 2 K, with emphasis in the “spin-gap” regime ($2 < T < 40$ K) [25]. Our study demonstrates the onset of subtle atomic displacements, concurrent with an unusual negative thermal expansion in the dimerized state, all postulating to delicate spin-lattice coupling effects for $T < 40$ K. This new knowledge on the SrCu$_2$(BO$_3$)$_2$ lattice, offers a valuable insight in view of future efforts aiming to understand how the ground state energy is minimized by lattice modifications pertaining to the rearrangement of the magnetic interactions among the Cu dimers.

2. Experimental

Single crystals of SrCu$_2$(BO$_3$)$_2$ have been grown from a Li$_3$BO$_3$-flux as described elsewhere [26]. A 4 g polycrystalline sample was produced from crashing the rods used for the single crystal growth. Neutron powder diffraction experiments were performed on the High-Resolution Powder Diffractionmeter (HRPD) and on the General Material Diffractometer (GEM) at the neutron spallation source ISIS (UK). The sample used for the present work was inserted in a flat rectangular sample holder (HRPD; 4 g powder) and in a 6 mm Vanadium can (GEM; 1 g powder). HRPD data were collected from room temperature to $T = 2$ K, with particular interest in the low-temperature region. For $T < 100$ K, temperature steps of 4 K were used, while for $T > 100$ K, the temperature was raised in steps of 50 K. Long counting time was allowed for data collected at 2, 100 and 295 K. Measurements on GEM were performed in the temperature range $2 < T < 40$ K, on warming with temperature intervals of 1 K and high statistics. In both cases a standard ILL Orange cryostat was used. The collected patterns were analyzed with the Rietveld method. Refinements of the nuclear structure were carried out with the GSAS program suite [27].

3. Results and discussion

From the crystallographic point of view, SrCu$_2$(BO$_3$)$_2$ shows a second-order structural phase transition at $T_S = 395$ K from space group $I4/mcm$ above $T_S$ to a non-centrosymmetric space group $I-42d$ below $T_S$ [24]. Below 395 K all our datasets could be refined with the proposed space group. Fig. 1 shows a representation of the structure as derived after Rietveld refinements of the room temperature HRPD data. Our structural analysis shows that layers extending in the $ab$-plane are formed by BO$_3$$^3$- groups and Cu$^{2+}$ ($S = \frac{3}{2}$) ions, while Sr$^{2+}$ ions separate two adjacent layers along the $c$-axis. The coordination of copper by the rigid BO$_3$ groups leads to
an pronounced angular distortion (corrugation) of the CuO$_4$ square below $T_c$, with important consequences on the effect of the magnetic anisotropy on the ground state properties. The nearest-neighbor ($m$) copper atoms form dimers of edge-sharing CuO$_4$ groups, which are not co-planar at $T < T_c$ and as that the Cu-BO$_3$ layer is not a mirror plane for the dimers, as it used to be above $T_c$. Each dimer is coordinated from both sides by the two symmetry equivalent oxygens of the borate group. The dimers are orthogonally arranged with respect to each other in a topologically equivalent Shastry–Sutherland lattice arrangement. In this lattice type each dimer becomes relatively strongly coupled to the two neighboring orthogonal dimers (next-nearest-neighbors $= m m n$) by super–superexchange interactions ($J_{2}$) via rigid BO$_3$ groups. Our structural analysis finds that these BO$_3$ groups do not show any appreciable temperature dependence in the $T$ range of interest. Indeed, the $B$–01 and $B$–02 distances remain at values of 1.372(1) and 1.378(1) Å, respectively, while in the low-$T$ region. The corresponding angles are also rather rigid, taking values of 122.90(5)° for 01–B–02 and 114.2(1)° for 02–B–02 (Fig. 1). Rigidity in planar triborate groups is frequently met in metal-borate systems. For example, in LiB$_3$O$_5$, triborate units composed of three inequivalent B–O bonds (1.349(5), 1.367(1) and 1.396(1) Å) are connected with flexible Li–O linkages that are responsible for the anisotropic thermal expansion of the lattice [35]. In the present case, with the rigid BO$_3$ interconnecting the dimers, we will show that the different expansion tendency of the CuO$_4$ structural units allows in the SrCu$_2$(BO$_3$)$_2$ subtle modifications that could optimise interactions of different nature, such as the magnetic exchange coupling (vide infra).

Other crystal system changes, which were unveiled by the high resolution of the HRPD diffractometer, include a significant broadening of the Bragg reflections, inferring to distortions due to microstrain. In order to properly take this into account, a model with anisotropic strain broadening based on Stephens formalism has been incorporated in the Rietveld refinements [28]. Within this formalism, the spacing $d$ between lattice planes for any given reflection defined by the Miller indexes $h k l$ is $1/d^2 = A h^2 + B k^2 + C l^2 + D h k + E h l + F k l$, where the capital case letters represent metric parameters of the reciprocal lattice. Strain broadening here is considered as a manifestation of the distribution of these parameters. We can therefore write the contribution to the broadening on a reflection $h k l$ due to strain as $\sigma^2(h k l)$. The variance matrix for a Gaussian distribution of these parameters can be expressed in the following way:

$$\sigma^2(h k l) = \sum_{\text{HKL}} S_{h k l}^2 h^2 k^2 l^2$$

with the term $S_{h k l}$ defined for $H+K+L=4$ ($H, K, L \geq 0$). For Laue symmetries other than -1 (triclinic), the symmetry imposes restrictions on the allowed $S_{h k l}$ terms. Since the Laue class of the structure for this compound is $4/m m m$ (tetragonal), only 4 independent coefficients are allowed (i.e. for a tetragonal symmetry: $A=B$, $D=E=F=0$ and the corresponding anisotropic strain parameters are $S_{400}=S_{040}$, $S_{202}=S_{022}$, $S_{004}=S_{040}$, $S_{220}$. The refinement with this model (including strain: $\chi^2=3.415$, Bragg $R$-factor=4.5%, without strain: $\chi^2=12.97$ and Bragg $R$-factor=10% at $T=2$K) showed large strain coefficients, such as $S_{400} \sim 1.77(4)$ and $S_{202} \sim 3.13(3)$, while others like the $S_{004}$ and $S_{220}$ parameters were found to be smaller ($\sim 2.28 \times 10^{-1}$) and $\sim 1.24 \times 10^{-1}$ (7), respectively). Based on this analysis, we also find that the lattice strain does not seem to exhibit significant temperature dependence within the $T$-range investigated. The enhanced $S_{h k l}$ parameters are an indication of defects or disorder, which in the present case appears mainly along the $c$-direction, as the Stephens coefficients with non-zero $l$ index are larger. This could be an effect of the corrugation of the $ab$-planes below the high-$T$ ($T_c$) structural transition. Importantly, the purpose of this study is to look for spontaneous changes in the crystal system by means of Rietveld refinements as accurate knowledge of the lattice symmetry determines the spin-anisotropies necessary to rationalise experimental observations, such as, forbidden singlet-triplet transitions in high-field ESR [29]. Along these lines it is worth noting that the data collected on the HRPD diffractometer (Fig. 2a), have revealed unusual negative thermal expansion of the lattice below $T \approx 40$K (Fig. 2a, inset). We argue that this is primarily due to the in-plane expansion (0.02%; vide infra), which overcomes a slight contraction along the $c$-direction. The quite unusual and puzzling behaviour of SrCu$_2$(BO$_3$)$_2$ around the $T=34$K region motivated us to study the subtle lattice changes in more detail and the results are discussed in the following paragraphs. Although the HRPD data provide reliable information on the general lattice modifications, the involved statistics do not allow for an accurate determination of the $T$-dependence of crystallographic

Fig. 2. Rietveld plots for (a) $T=100$K diffraction pattern of SrCu$_2$(BO$_3$)$_2$ collected on the HRPD diffractometer. Inset: Full temperature evolution of the unit cell volume. (b) $T=2$K diffraction pattern of SrCu$_2$(BO$_3$)$_2$ collected on the GEM diffractometer. The black dots represent the data, red line is the calculated pattern fitted to the data, while the blue line at the bottom of the plot is the difference between calculated and observed. The green vertical marks indicate the position of the Bragg reflections. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.
parameters, such as bond lengths, bond angles and thermal parameters, which can all reflect local lattice adjustments.

In order to derive precise crystallographic information and observe structural deformations pertaining to the spin-gap region, datasets were recorded on the GEM diffractometer (Fig. 2b) below $T=40$ K. We observe an expansion in the $ab$-plane and contraction in the $c$-axis (corresponds to volume expansion of 0.02%; Fig. 3), in agreement with the earlier HRPD work. Table 1 summarizes the lattice parameters and atomic positions from the $T=2$ and 40 K GEM datasets, respectively. Fig. 4a shows the temperature dependence of the intra-dimer (Cu1–O1–Cu2) angle (Fig. 1). This angle significantly increases from about 98.02(7)° at 40 K to about 98.49(7)° between adjacent layers, while the long inter-dimer distances (Cu2–Cu4; Fig. 5b) remain almost constant in the $ab$-plane and there is a contraction in the $c$-plane (Fig. 3a), in agreement with the earlier HRPD work. Table 1 summarizes the lattice parameters and atomic positions from the $T=2$ and 40 K GEM datasets, respectively. Fig. 4a shows the temperature dependence of the intra-dimer (Cu1–O1–Cu2) angle (Fig. 1). This angle significantly increases from about 98.02(7)° at 40 K to about 98.49(7)° at 2 K. At the same time, the intra-dimer Cu1–Cu2 distance (Fig. 1) expands, changing from 2.916(2) Å at 40 K to 2.930(2) Å at 2 K (Fig. 4b).

The increase of the Cu1–Cu2 distance is directly related to the lattice expansion in the $ab$-plane (Fig. 3a). This is partially balanced by a shortening of the Cu1–Cu3 inter-dimers distances (Fig. 4c). Very interestingly, we observed that the bending angle between the CuO4 groups (Fig. 4d), defined by the angle formed by the O1–Cu2–O1' bond, decreases from 2.899(3) Å (namely slightly shorter than in SrCu2(BO3)2), while the O–Cu–O angles are much closer to 90° (i.e. 89.89(3))° with respect to those (i.e. ~81.28(7))° measured in SrCu2(BO3)2. The geometry of the staggered CuO4 groups in Bi2CuO4 does not support cation–anion–cation exchange interactions, but super–superexchange interactions involving two oxygen atoms. Such interactions have been invoked as being responsible for short-range order along the chains. These short-range correlations determine the observed antiferromagnetic behaviour that relates Cu atoms belonging to different chains.

Let us now consider the effect of inter- and intra-dimer exchange interactions on the lattice and the distortions therefore observed in SrCu2(BO3)2. Below 34 K, the leading interaction that modifies the nuclear structure of SrCu2(BO3)2 is the isotropic magnetic exchange. Indeed, the opening of the Cu1–O1–Cu2 angle (Fig. 4a) and the increase of the Cu1–Cu2 dimer distances (Fig. 4b), while BO3 side groups remain unmodifed at low-T (vide infra), suggest a strengthening of the intra-dimer superexchange ($J_1$). If we assume AFM spin arrangement of the Cu moments within each dimer, the application of Goodenough–Kanamori–Anderson (G–K–A) rules [30] would suggest enhanced $nn$ ($J_n$) exchange integrals (Fig. 1). Interestingly, in SrCu2(BO3)2, the inter-dimer exchange path (which contains the rigid BO3 groups) shrinks (Fig. 4c), showing an opposite trend compared to the intra-dimer one that elongates (Fig. 4b). All the lattice changes occur while crossing-over into the spin-gap regime. We therefore assume that at low enough temperature significant spin–lattice coupling is established when the concentration of triplets increases (with increasing $T$). This will tend to minimize the intra-dimer exchange; hence the shrinkage of the lattice (due to a reduction of the Cu–O–Cu angle) with increasing temperature, before the natural thermal expansion takes over. Consequently, the enhanced spin–lattice coupling leads to the observed negative thermal expansion of 0.02% in the $ab$-plane (Fig. 3).

In support to this behaviour comes a recent synchrotron X-ray diffraction study where lattice contraction in SrCu2(BO3)2 has been also observed when the strength of an intense applied magnetic field is raised at low-temperatures (~1.5 K). This tuneable

### Table 1

<table>
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<th>x/a</th>
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<td>0.2949(8)</td>
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<tr>
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<tr>
<td>O2</td>
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<td>0.2591(2)</td>
<td>1.0</td>
<td>0.10(2)</td>
</tr>
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(a) $T=2$ K: Lattice parameters: $a = 8.98493(6)\,\text{Å}$, $c = 6.64117(8)\,\text{Å}$, $V = 536.135(8)\,\text{Å}^3$. Weighted profile $R_{wp}$ (%) = 3.95, Profile $R_p$ (%) = 3.70, Bragg $R$-factor (%) = 4.47, $\chi^2$ = 13.99. (b) $T=40$ K: Lattice parameters: $a = 8.98354(6)\,\text{Å}$, $c = 6.62429(8)\,\text{Å}$, $V = 536.059(9)\,\text{Å}^3$. Weighted profile $R_{wp}$ (%) = 3.92, Profile $R_p$ (%) = 3.76, Bragg $R$-factor (%) = 4.3, $\chi^2$ = 14.71. Estimated standard errors at the last significant digit are given in parenthesis.

![Fig. 3](image_url) Temperature evolution of the Rietveld refined lattice parameters in the low-temperature range ($2 \leq T \leq 40$ K; GEM diffractometer) of the SrCu2(BO3)2. (a) The tetragonal $a$ and $b$ crystallographic directions; an unusual in-plane expansion is resolved. (b) The $c$ crystallographic direction; an out-of-plane contraction takes place. (c) The unit cell volume; negative thermal expansion is uncovered within the spin-gap region.
parameter also increases the population of triplets as does the temperature increase [34] and the authors reported the observation of a close relationship between the lattice constants and magnetization. They found a variation of the in-plane lattice constant with an applied field, $B_i$, of the order of $a/B_0 = [a(T=2K)/a(T)]/a(B_i)/a(T_0)$ at 30 T, 1 $\times$ 10$^{-4}$ at 35 T. Very interestingly, their findings are in agreement with our structural measurements for the temperature dependence of the basal plane lattice parameters, which result in changes of the same order of magnitude, namely, 0.5 $\times$ 10$^{-4}$ at 7 K, 1 $\times$ 10$^{-4}$ at 10 K and 1.2 $\times$ 10$^{-4}$ at 35 K.

Together with the effect of the frustrated, isotropic superexchange interactions ($J_1$, $J_2$) on the lattice, it is worth considering the influence of two possible weaker interactions to the spin gap, namely the inter-layer coupling $J_3$ and the magnetic anisotropy. The latter involves the antisymmetric Dzyaloshinsky–Moriya interaction $D(S_i \times S_j)$, where $S_i$, $S_j$ represent the spins at neighboring sites [23], that justifies the fine structure of the excited triplet state and its unusual magnetic field dependence [31,32]. In the SrCu$_2$(BO$_3$)$_2$ structure, a center of inversion of the dimer bond forbids the intra-dimer DM interaction ($T>T_g$), and instead the inter-dimer out-of-plane DM interaction evolves as the dominant one. When we lower the temperature, the inversion center of symmetry is lost at the $I_4/mcm$ to $I_42m$ structural transition [11,24] and another DM component may play a role. Namely the $nn$ intra-dimer DM interaction can become important, which has been suggested as a pathway to account for forbidden singlet–triplet transitions in high-field ESR [29,33]. From the analysis of the present NPD data ($T<T_g$), we find that the lattice symmetry does not preclude $nn$ DM interactions. When we enter the spin-gap region ($T<T_g$), the in-plane structure becomes more rigid due to the strengthening of intra-dimer interactions (vide supra). Such a modification of the crystal lattice leads to a decrease of the observed planar buckling, but the mirror plane lost below $T_g$ is not recovered, meaning that $nn$ DM interactions are still a feasible mechanism.

Furthermore, we realize that weak three-dimensional exchange interactions can also develop in the system through the flattening of the $ab$-plane ($<34$ K), as evidenced by the increase of the Cu3–Cu5 ion distances (Fig. 5a) that correspond to the short inter-dimer separation between the layers. On the contrary, the long inter-dimer distances (Cu2–Cu4; Fig. 5b) remain almost unaltered below $T=34$ K. The two types of inter-layer couplings ($J_{1,2}$; Fig. 1b) that are established herein, have been estimated to range from $J_{1,2}/J_{1}=0.094$ to 0.21 [15,16]. As they are relatively weaker with respect to the corresponding in-plane exchange
integrals, they are expected to play a minor role in the observed structural distortions.

The current NPD analysis finds small crystal system changes that do not violate restrictions posed by the tetragonal $I-42m$ lattice symmetry of SrCu$_2$(BO$_3$)$_2$. A comprehensive theoretical study, based on the structural modifications described in this work is desirable. We expect that it will improve the understanding of the temperature evolution of the exchange coupling integrals and the role of magnetic anisotropy within the spin-gap region.

4. Conclusions

We performed extensive high-resolution, high-statistics neutron powder diffraction measurements on the two-dimensional quantum antiferromagnet SrCu$_2$(BO$_3$)$_2$, between room temperature and down to 2 K. Subtle spin–lattice coupling was unveiled in the low-temperature region ($< 34$ K), where the spin-singlet state populates and characterises the ground state properties. The Rietveld analysis of the NPD data revealed an unusual negative thermal expansion of the lattice, which reflects upon subtle lattice adjustments without space group symmetry ($I-42m$) change. The dimerization of the Cu–Cu ions, mapping onto an orthogonal spin-dimer system and the concurrent widening of the angle connecting nearest-neighbour Cu sites, suggests the strengthening of the intra-dimer antiferromagnetic interactions. We find that the increase in the intra-dimer separation changes quite significantly the structure. The novel orthogonal arrangement of the dimers leads to a net expansion in the $ab$-plane and a reduction to the in-plane inter-dimer distances. These lattice distortions that take place at low enough temperatures ($< 34$ K) are not exclusive to in-plane modifications. Importantly, the buckling of the copper-borate planes is also modified. The structural analysis suggests that the out-of-plane coupling strengthen somehow, due to the shrinkage along the $c$-direction. It reflects a more three-dimensional type of behaviour for the SrCu$_2$(BO$_3$)$_2$ lattice within the spin-gap temperature region. At low-temperatures ($< 34$ K), the rules posed by the crystal symmetry ($I-42m$) on the Cu dimers allow for Dzyaloshinskyy–Moriya (DM) coupling of the magnetic moments. Our analysis suggests that DM interactions remain a crucial spin anisotropy for understanding the intriguing SrCu$_2$(BO$_3$)$_2$ magnetic behaviour.

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Appendix. Supporting Information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.09.017.

References

[25] For clarity in the discussion we define the region below $T=34$ K as the ”spin gap” regime to address the structural and magnetic changes that occur as a consequence of the modification in population of the singlet and triplet states. We therefore use this terminology throughout the manuscript.