The Shastry-Sutherland Compound SrCu$_2$(BO$_3$)$_2$

Studied up to the Saturation Magnetic Field

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We report ultrasound velocity and magnetostriction results for the orthogonal-dimer antiferromagnet SrCu$_2$(BO$_3$)$_2$ up to the saturation magnetic field. In addition to anomalies that can be associated to plateaus with fractional magnetization $M/M_s = 1/8, 1/4, 1/3, 2/5, \text{ and } 1/2$, we have detected higher-field sound-velocity and magnetostriction anomalies at 116, 127, and 139 T. Strikingly, the anomalies of the sound velocity of the $c_{ab}$ acoustic mode are very much plateau dependent, with a huge decrease by $-50\%$ in the $1/2$ plateau state due to the tetragonal-to-orthorhombic instability triggered by the triplet crystallization into a checkerboard pattern. This effect, as well as the high-field anomalies, can be well accounted for by tensor-network calculations (iPEPS) of the Shastry-Sutherland model. We conclude in particular that the anomaly at 139 T corresponds to the saturation of magnetization, and we suggest that the other two anomalies at 116 and 127 T are related to supersolid phases whose energies are nearly degenerate in this field range.

I. INTRODUCTION

The discovery of a sequence of magnetization plateaus in SrCu$_2$(BO$_3$)$_2$ (SCBO), stabilized at fractional magnetization values, is a milestone in quantum spin physics [1,2]. In this material, Cu$^{2+}$ ions with spin $S = 1/2$ arrange in an orthogonal-dimer geometry known as the Shastry-Sutherland lattice [Figs. 1(a, b)] [3, 6]. The effective Hamiltonian including intra- and inter-dimer interactions ($J$ and $J'$, respectively) and the Zeeman term is defined by

$$
\mathcal{H} = J \sum_{\langle ij \rangle} S_i S_j + J' \sum_{\langle\langle ij \rangle\rangle} S_i S_j - h \sum_i S_i^z. \tag{1}
$$

The competing antiferromagnetic (AFM) couplings ($J$ and $J'$) result in a geometrical frustration, giving rise to various phases depending on the ratio $J'/J$ and magnetic field $h$ [4]. The exchange parameter ratio for SCBO at ambient pressure is estimated to be $J'/J \sim 0.63$ from the magnetization measurement up to 118 T [3]. However, the pantograph-like magnetostriction, which modulates the Cu-O-Cu angle and, hence, the superexchange interaction, can change the ratio in applied magnetic fields [5, 16]. At low temperatures, SCBO shows a fascinating magnetization curve with multiple anomalies, the most prominent ones are related to the plateau phases at 1/8, 2/15, 1/6, 1/4, 1/3, 2/5, and 1/2 of the saturation magnetization $M_s$ [3, 17, 18]. In the plateau regions, triplets (or bound states of triplets for the low-field plateaus) crystallize into magnetic superstructures [20, 22] as a result of the effective repulsion and the localized nature of triplets inherent to the frustrated geometry [3, 23, 26]. So far, no experimental investigation up to the saturation magnetization has been reported.

In this paper, we present the results of ultrasound and magnetostriction measurements up to 150 T, reaching to the saturation field. For studying the magnetism
of SCBO at extremely high magnetic fields, the ultrasound and magnetostriction are powerful techniques due to presence of the spin-strain interactions. Furthermore, the sensitivity of these techniques is maximal at the top of the pulsed field, where the sensitivity is strongly reduced for the magnetization measurements \cite{27}. Besides, the earlier studies have pointed out that the spin-lattice coupling plays an important role for the high-field properties of SCBO \cite{15,17,28,31}. In particular, the \(c_{66}\) mode (with \(\pm \epsilon_{xy}\) strain) shows extremely large anomalies. In this study, we discuss the magneto-structural properties of SCBO at ultrahigh magnetic fields supported by the theoretical calculations based on the infinite projected entangled pair state (iPEPS) tensor-network algorithm \cite{32,33}. The elastic properties of novel supersolid phases above 100 T are discussed in terms of the spin-lattice coupling.

II. EXPERIMENTAL METHOD

The pulsed magnetic fields up to 150 T were generated with help of the vertical single-turn-coil system (STC) in the ISSP, University of Tokyo \cite{35}. We used a liquid \(^4\)He bath cryostat to keep the sample at 3.2–4.2 K. We note that the sample temperature can change due to the magnetocaloric effect during the pulsed field (\(\sim 6 \mu s\)) \cite{17,30}. High-quality single crystals of SCBO were grown by a traveling solvent floating zone method \cite{36}. We used the one (\(2 \times 1 \times 1 \text{ mm}^3\)) for the ultrasound and another one (\(2 \times 1 \times 0.3 \text{ mm}^3\)) for the magnetostriction measurement. Magnetic fields were always applied along the \(c\) axis in our experiments.

We performed the ultrasound measurements by using the continuous-wave excitation technique \cite{37}. Ultrasound waves with the frequency of 20–40 MHz were excited by a \(\text{LiNbO}_3\) transducer attached to the surface of the crystal. The transmitted waves were detected by another transducer and recorded by a digital oscilloscope. The recorded signals were analyzed by using the numerical lock-in technique, and the phase change was converted to the relative change of sound velocity \(\Delta v/v_0\). With this technique, one can obtain reliable results around the peak of the pulsed field where the field sweep rate slows down. Therefore, we repeated the measurements with different peak fields and extracted the reproducible part of the results. We also performed the ultrasound measurements up to 83 T by using the ultrasound pulse-echo technique with a dual-pulse magnet in HLD, Dresden \cite{38}. We measured two in-plane modes, \(c_{66} (k\|x, u\|y)\) and \(c_{11} (k\|u, u\|y)\), where \(k\) (\(u\)) is the propagation (displacement) vector.

We performed the magnetostriction experiments using the Fiber-Bragg grating (FBG) fixed onto the crystal and the optical filter method \cite{39}. When the sample length changed, the Bragg wavelength of the reflected light also changed. By using a band-pass filter with a band edge close to the Bragg wavelength, the reflection wavelength shift was detected as an amplitude change. This scheme allows us to measure magnetostriction at a high speed of 100 MHz. We used an amplified spontaneous emission source as an incident broadband near-infrared light source. In this study, we fixed the FBG using the low-temperature glue SK-229 to detect the longitudinal magnetostriction along the \(c\) axis, \(L_c\). In addition, the fiber and sample were put deep inside a vacuum grease to attenuate the sample vibration caused by the magneto-structural phase transitions \cite{40,41}. Because of the large amount of grease coupled to the FBG, the detected magnetostriction was reduced to \(\sim 20\%\) of the reported value \cite{17}. Nevertheless, the obtained magnetostriction was qualitatively reproducible and reflected the magnetic-field-induced phase transitions.

III. EXPERIMENTAL RESULTS

Figure 2 shows a summary of the ultrasound and magnetostriction results up to the ultrahigh field of 150 T. For comparison, the magnetization curve at 2.1 K \cite{3} is shown in Fig. 2(c) with bars representing the regions of magnetization plateaus. For reproducibility and raw data, see Supplemental Material (SM) \cite{42}.

First, we discuss the results of the sound velocity. Figure 2(a) shows the relative changes of the sound velocity \(\Delta v/v_0\) for the \(c_{11}\) mode (multiplied by 10) and the \(c_{66}\) mode. The results obtained by using the non-destructive magnet are shown by the black curves. \(\Delta v/v_0\) is significantly larger for the \(c_{66}\) than \(c_{11}\) mode, which is consistent with the previous study \cite{29}. Clear anomalies are observed at 27, 33, 40, and 74 T, corresponding to the onsets of the 1/8, 1/4, 1/3, and 2/5 plateau phases, in line with published high-field results \cite{3,17}. The results above the 1/2 plateau are obtained by the STC experiments (colored curves). Therefore, the experimental error (\(\pm 10\%\) of \(\Delta v/v_0\)) is larger than that obtained in a non-destructive pulsed magnet (\(\pm 3\%\) of \(\Delta v/v_0\)). Nevertheless, the relative changes in \(\Delta v/v_0\) are reliable and qualitatively well reproduced. The sound velocity of the \(c_{66}\) mode stays constant at \(\Delta v/v_0 = -50\%\) in the 1/2 plateau phase. This is a surprising result because such a large softening is usually observed at the phase boundary when a soft mode leads to a lattice distortion \cite{43}. The strong softening persists up to 116 T, which is slightly higher than the end of the 1/2 plateau (108 T) reported by the magnetization measurement \cite{3}. At 116 T, \(\Delta v/v_0\) shows a drastic increase. Another anomaly is observed at 126 T, where the slope of \(\Delta v/v_0\) changes. One more anomaly is detected at 140 T, where \(\Delta v/v_0\) discontinuously increases and saturates at the level of \(+20\%\). In contrast to the \(c_{66}\) mode, the \(c_{11}\) mode reveals no clear anomaly above 80 T within our experimental resolution.

Figure 2(b) shows two magnetostriction curves measured along the \(c\) axis. The results exhibit features similar to those of the magnetization; both start to increase when the spin gap closes (\(\sim 25\) T) and stay approxi-
approximately constant in the plateau phases. Here, we comment on the reproducibility of our magnetostriction results. As the previous study shows [17], the magnetostriction strongly depends on the experimental setting and the strain between the FBG and the sample. Indeed, we also find that the results vary slightly depending on the glue and the surrounding grease. Although the overall magnetostriction depends on the setting, the transition field detected by this technique is well reproducible. Therefore, in this study, we only focus on the critical fields and do not discuss the magnitude of the magnetostriction. Above the 1/2 plateau, we detect four critical fields and do not discuss the magnitude of the results obtained with the nondestructive magnet at 1.5 K and the STCs at 3.2 K are shown by the black and colored curves, respectively. The purple, green, orange, yellow, cyan curves represent the results up to 108 T. The results are multiplied by 10. The results obtained with the nondestructive magnet at 1.5 K and the STCs at 3.2 K are shown by bars. Anomalies above the 1/2 plateau are denoted by arrows.

FIG. 2. The ultrahigh-field data \((H//c)\) obtained in SrCu2(BO3)2. (a) Relative change of the sound velocity for the \(c_{11}\) and \(c_{66}\) acoustic modes. The results for the \(c_{11}\) mode are multiplied by 10. The results obtained with the nondestructive magnet at 1.5 K and the STCs at 3.2 K are shown by the black and colored curves, respectively. The purple, green, orange, yellow, cyan curves represent the results up to the maximum fields of \(\sim 150, 130, 120, 70, 30\) T, respectively. (b) Magnetostriction along the \(c\) axis measured at 4.2 K. (c) Magnetization along the \(c\) axis measured at 2.1 K. The plateau field regions suggested by the magnetization measurement are shown by bars. Anomalies above the 1/2 plateau are denoted by arrows.

Table I summarizes the critical fields obtained by the ultrasound, magnetostriction, and magnetization experiments. The critical-field notations \((H_{c6}, H_{c7}, H_{c8}, H_{c9})\) are termed after Ref. [3]. The critical-field values agree well considering the error range of the STC experiments. The only discrepancy is that the anomaly at 108 T is missing in the ultrasound results. This anomaly corresponding to the end of the 1/2 plateau is observed in both magnetization and magnetostriction. Note that the experimental conditions (sample cooling and sweep rate) are very similar for these three experiments. Therefore, it suggests that the symmetric modes \((c_{11} \text{ and } c_{66})\) are not sensitive to the transition at 108 T. The origin of the observed anomalies is discussed below.

### Table I. Critical fields with error ranges in the unit of Tesla

|        | \(H_{c6}\) | \(H_{c7}\) | \(H_{c8}\) | \(H_{c9}\) |
|--------|------------|------------|------------|------------|
| Ultrasound | –         | 116(3)     | 126(3)     | 140(2)     |
| Magnetostriction | 108(2) | 116(2)     | 128(3)     | 138(3)     |
| Magnetization  | [3]       | 108(1)     |            |            |

IV. THEORETICAL APPROACH

We have used iPEPS to map out the phase diagram at high magnetic fields, complementing previous results at low \([50–52]\) and intermediate fields \([53–55]\). An iPEPS is a variational tensor network ansatz to represent 2D ground states in the thermodynamic limit \([32–34]\) and can be seen as a higher-dimensional generalization of matrix product states. The ansatz consists of a unit cell of tensors which is periodically repeated on the infinite 2D lattice. Here we use one tensor per dimer and unit cells of different sizes to capture the relevant magnetic structures. The accuracy of the ansatz is systematically controlled by the bond dimension \(D\) of the tensors. The optimization of the variational parameters is done based on an imaginary time evolution using a simple update \([44]\) and cluster update \([45]\) approach, which provides good estimates of ground state energies while being computationally affordable even for very large unit cell sizes. The approximate contraction of the 2D tensor network is done by a variant \([46, 47]\) of the corner-transfer matrix method \([48, 49]\), where the contraction dimension \(\chi\) is kept large enough so that contraction errors are negligible. For more details on the iPEPS approach we refer to Refs. \([50–52]\).

V. THEORETICAL RESULTS

In Fig. 3, we present the phase diagram as a function of \(J'/J\) between the 1/2 plateau and full saturation, for values of \(J'/J\) in the vicinity of the predicted value \(J'/J = 0.63\) for SCBO from Ref. [3]. The data has been obtained for a bond dimension \(D = 8\) and cluster update...
optimization, which is sufficiently large so that finite-\(D\) errors on the phase boundaries are small (of the order of the symbol sizes). Representative spin patterns of the phases are also shown in Fig. 3. Besides the familiar 1/2 plateau phase, we find different types of supersolid phases (SSPs), i.e. phases which simultaneously break translational symmetry and the U(1) symmetry associated with the total \(S^z\) conservation. They all exhibit a diagonal stripe pattern with a certain period.

Above the 1/2 plateau the dominant phase is the 1/3 SSP, which has a period 6 and which can also be found at lower fields above the 1/3 plateau (hence the name 1/3 SSP, see Ref. [3]). Within the 1/3 SSP, there are two distinct regions which we call type a and type b. The former has 2 different spin directions, whereas the latter has 6. In between the 1/2 plateau and the 1/3 SSP for \(J'/J \lesssim 0.63\), an extremely narrow period-10 SSP appears, which is energetically very close to their neighboring phases. At higher magnetic fields we find a transition into a period-14 SSP before reaching saturation. Close to saturation, the energies of the competing states get very close. At larger values of \(J'/J \sim 0.68\) a period-8 SSP is stabilized before saturation. We did not find evidence of another plateau above the 1/2 plateau, although a 7/8 plateau gets energetically close to the supersolid phases, especially at larger values of \(J'/J\).

In Fig. 4 the magnetization curve for \(J'/J = 0.63\) together with the energy differences of the competing states is shown, where the vertical dashed lines indicate the phase boundaries. Converted to real units [3], we find that the 1/2 plateau terminates at 106 T, with a jump in magnetization to the extremely narrow period-10 SSP, followed by the 1/3 SSP. The location of this transition is compatible with \(H_{c6}\) from the magnetostriction and magnetization measurements. The transition between the two 1/3 SSPs is found at 122 T (there is no anomaly observed in experiments at this value which could be because the two 1/3 SSPs are very similar states). The transition into the period-14 SSP occurs around 128 T.
TABLE II. First and second derivatives of the energy with respect to the strain \( \varepsilon_{xy} \) (\( c_{66} \) mode) obtained with iPEPS (\( D = 6 \)). The iPEPS estimates of \( \Delta c/c_0 \) in the fourth column have been obtained based on a least-squares fit of the form \( \lambda_1 E' + \lambda_2 E'' \) to the experimental values of \( \Delta c/c_0 \).

| \( M/M_a \) | \( \Delta c/c_0 \) | \( \Delta c/c_0 \) | \( \Delta v/v_0 \) | \( \Delta v/v_0 \) |
|-------------|-----------------|-----------------|-----------------|-----------------|
| iPEPS       | Exp.            | iPEPS           | Exp.            | iPEPS           |
| 1/4         | -0.051          | -0.31           | -0.34(5)        | -0.16           |
| 1/3         | 0 -0.18         | -0.08           | -0.06(4)        | -0.04           |
| 1/2         | -0.23           | -0.034          | -0.74           | -0.73(11)       |

which coincides with \( H_{c8} \). Finally, saturation is reached at 137 T, in close agreement with the experimental values of \( H_{c9} \).

VI. DISCUSSION

A. Sound velocity of the plateau phases

First, we quantitatively discuss the drastic sound-velocity change of the \( c_{66} \) mode. The sound velocity \( v \) is a thermodynamical quantity, related to the elastic constant \( c \), as \( c = \rho v^2 \). Here, \( \rho \) is the mass density. The elastic constant is the second derivative of the free energy with respect to the strain. In SCBO, strain modulates the Cu-O-Cu angle and exchange coupling of the dimers, leading to a modulation of the magnetic free energy. Depending on the elastic modes (\( c_{66} \) and \( c_{11} \)), the exchange modulation acts on dimers asymmetrically and symmetrically, respectively [Figs. 1(c, d)]. For the case of the \( c_{66} \) mode with \( \varepsilon_{xy} \), the Cu-O-Cu angle of the horizontal (vertical) dimer decreases (increases), leading to the reduced (enhanced) AFM interaction. This bond alternation naturally stabilizes the 1/2 plateau phase with the checkerboard pattern; i.e. vertical dimers with (almost) aligned spins and horizontal dimers with predominantly singlets (or vice versa). This is in strong contrast to the 1/3 plateau which exhibits polarized spins on both the vertical and horizontal dimers [separated by two rows with dimers with opposite spins on each dimer \[4\)]. This odd periodicity leads to a cancellation of contributions when computing the derivative, leading to a value close to zero. The 1/4 plateau exhibits an even periodicity (every fourth diagonal row exhibits almost polarized spins), leading to a finite first derivative, albeit with a smaller magnitude than the 1/2 plateau, as observed also in the experiment. At saturation, the state is a product state (all spins aligned) and the derivatives with opposite signs cancel each other exactly.

Table 1 summarizes the first and second derivatives of the free energy (\( E' \) and \( E'' \)) for the \( c_{66} \) mode. Here, we have evaluated the energy shift with respect to \( \varepsilon_{xy} \), which reduces (enhances) the AFM exchange coupling of the horizontal (vertical) dimer. As discussed, \( E' \) is much larger in the 1/2 plateau than in other plateau phases. This is a common feature with the experimental \( \Delta v/v_0 \), where the sound velocity significantly decreases in the 1/2 plateau but does not in the 1/3 plateau. In fact, the experimental \( \Delta v/v_0 \) (and \( \Delta c/c_0 \)) of the major plateau phases at 1/4, 1/3 and 1/2 is nearly proportional to \( E' \) (see the second, fifth, and seventh columns of Table II), suggesting that \( E' \) gives a major contribution to the elastic constant as compared to \( E'' \) although the elastic constant is the second derivative of the free energy. In fact, \( E' \) contributes to the elastic constant via the anharmonic potential of the lattice (see SM for details \[12\]). This anharmonicity is specifically important for the 1/2 plateau phase because the triplet crystallization into the checkerboard pattern leads to the cooperative exchange striction from tetragonal to orthorhombic. Because of this exchange striction, Cu\(^{2+}\) ions move from the equilibrium positions at zero field to strained positions where the magnetic superstructure is better stabilized. At the strained position, the effect of the anharmonic potential becomes relevant, which is a key to connect \( E' \) and the elastic constant. Including the first- and second-derivatives contributions as \( \lambda_1 E' + \lambda_2 E'' \), the experimental \( \Delta v/v_0 \) is reasonably explained (see the sixth and seventh columns of Table II). The coefficients \( \lambda_1 \) and \( \lambda_2 \) are optimized by a least-squares fit.

B. High-field supersolid phases

The iPEPS calculation predicts four SSPs between the 1/2 plateau and the saturation. Even if \( J'/J \) changes under high fields because of the exchange striction, the phase boundary does not change greatly. In our experiments, the period-10 SSP and the transition from the 1/3 plateau type b to type a would not be detected because of the limited resolution and precision. Thus, we focus on the major phase boundaries, the end of the 1/2 plateau, the end of the 1/3 SSP, and the saturation field. The latter two are detected in both ultrasound and magnetostriiction experiments as \( H_{c8} \) and \( H_{c9} \). The quantitative agreement between the experiment and theory is excellent considering the experimental challenges at ultrahigh magnetic fields. The slight difference in the saturation field might be due to the magnetic-field dependence of \( J \).

The assignments of the lower-field boundaries \( H_{c6} \) and \( H_{c7} \) require careful discussions. The transition at \( H_{c6} \) is the end of the 1/2 plateau, where magnetization starts to increase discontinuously. This anomaly is observed in the magnetostriiction and magnetization experiments but is not detected in the ultrasound experiment. Another transition at \( H_{c7} = 116 \) T is observed both in ultrasound and magnetostriiction experiments but is not predicted by the iPEPS calculation. Experimentally, the \( \Delta v/v_0 \) of the \( c_{66} \) mode shows a drastic increase at \( H_{c7} \) [Fig. 2(a)].

From the experimental point of view, the transition from the 1/2 plateau to the 1/3 SSP, where the magnetic unit cell drastically reconstructs, should be detected by
the ultrasound technique. The ultrasound technique is generally sensitive to this kind of symmetry change at phase transitions [31]. Indeed, the calculated $E'$ is significantly larger in the 1/2 plateau because of the checkerboard pattern of triplets with the even period, while it is almost cancelled with the odd period of the 1/3 SSP. The ultrasound results without anomaly at $H_{c6}$ suggest that another SSP with an even period might appear as an intermediate phase between the 1/2 plateau and the 1/3 SSP. One possible scenario to explain the experimental results is that a 1/2 SSP appears at $H_{c6}$ just above the 1/2 plateau. In this case, the translational symmetry is the same for the 1/2 phases, and the calculated $\lambda_1 E' + \lambda_2 E''$ takes similar values. Thus, the ultrasound technique might be less sensitive to detect the transition from the 1/2 plateau to a 1/2 SSP. In contrast, the transition from a 1/2 SSP to the 1/3 SSP would be clearly detected because the magnetic unit cell drastically changes. The anomaly at $H_{c7}$ might correspond to this phase transition.

From the theoretical point of view, one can identify a metastable 1/2 SSP, but it is higher in energy than the 1/3 SSP for $J'/J \sim 0.63$. Therefore, the simple Shastry-Sutherland model does not explain the proposed scenario. To stabilize the 1/2 SSP, some additional terms need to be included in Eq. (1). One magnetic interaction neglected in the iPEPS is the interlayer coupling [53, 54]. Since the interlayer coupling is AFM, it is energetically not favorable to have two dimers of aligned spins on top of each other. Thanks to the checkerboard structure of the 1/2 plateau and 1/2 SSP, it is possible to always have a polarized dimer on top of a singlet dimer in 3D, leading to lower interlayer energy compared to that of the 1/3 SSP. The same holds true for the 1/2 SSP with the checkerboard-like structure, indicating that the 1/2 SSP could be stabilized with this term. Since the method used in the present work, iPEPS, is a purely two-dimensional approach, the inclusion of the interlayer coupling is left for future work. Another important magnetic interaction is the Dzyaloshinskii-Moriya (DM) term, which stabilizes canted spin orientations like in SSPs. However, this term would stabilize both the 1/2 SSP and the 1/3 SSP similarly. Thus, the DM term would not change the relative stability of these phases. Finally, the last term which might be relevant for the 1/2 plateau and SSP is the spin-lattice coupling term [55]. In these phases, the checkerboard pattern of triplets leads to a tetragonal-orthorhombic instability of the lattice. The orthorhombic distortion alternatively modulates the intra-dimer coupling $J$, stabilizing the magnetic energy at the expense of the elastic energy. This energy gain might be sufficiently large to stabilize the 1/2 SSP compared to the 1/3 SSP. Further work is needed to fully understand how to improve the agreement between experiment and theory in this field range.

VII. CONCLUSION

In this study, we have discussed the ultrahigh-field properties of SCBO, reaching magnetic saturation for the first time. Above 100 T, our ultrasound and magnetostriction experiments have detected four anomalies at $H_{c6} = 108$, $H_{c7} = 116$, $H_{c8} = 127$, and $H_{c9} = 139$ T. Quite remarkably, the ultrasound results reveal a very significant softening of the $c_{66}$ acoustic mode in the 1/2 plateau phase. Most of these results can be understood as consequences of the peculiar geometry of the layers of SCBO, as shown by a careful comparison with the results of iPEPS simulations of the Shastry-Sutherland model. In particular, the anomalous softening of the $c_{66}$ acoustic mode in the 1/2 plateau phase as compared to the other plateaus can be attributed to the tetragonal-orthorhombic instability triggered by the checkerboard pattern of triplets in this plateau. Besides, the iPEPS results clearly identify $H_{c7}$ as the saturation field. Furthermore, iPEPS simulations of the Shastry-Sutherland finds a sequence of competing SSPs between the 1/2 plateau and saturation, suggesting that the anomalies in this field range are due to transitions between such SSPs, with in particular a transition between a 1/3 SSP and a period-14 SSP at a field in good agreement with $H_{c8}$. At lower field, the absence of ultrasound anomaly at the end of the 1/2 plateau at $H_{c6} = 108$ T suggest that the 1/3 SSP only sets in at $H_{c7} = 116$ T, with possibly a 1/2 SSP in between. This assignment needs to be finalized however since the 1/2 SSP is only metastable for the Shastry-Sutherland model. Further work is needed to check if additional interactions such as interlayer or spin-lattice coupling can stabilize this phase. This goes beyond the scope of the present paper however.

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[1] H. Kageyama, K. Yoshimura, R. Stern, N. V. Mushnikov, K. Onizuka, M. Kato, K. Kosuge, C. P. Slichter, T. Goto, and Y. Ueda, Exact dimer ground state and quantized
magnetization plateaus in the two-dimensional spin system SrCu$_2$(BO$_3$)$_2$. Phys. Rev. Lett. 82, 3168 (1999)

[2] K. Onizuka, H. Kageyama, Y. Narumi, K. Kindo, Y. Ueda, and T. Goto, 1/3 magnetization plateau in SrCu$_2$(BO$_3$)$_2$ -stripe order of excited triplets-, J. Phys. Soc. Jpn. 69, 1016 (2000)

[3] Y. H. Matsuda, N. Abe, S. Takeyama, H. Kageyama, P. Corboz, A. Honecker, S. R. Mannmana, G. R. Foltin, K. P. Schmidt, and F. Mila, Magnetization of SrCu$_2$(BO$_3$)$_2$ in ultrahigh magnetic fields up to 118 T, Phys. Rev. Lett. 111, 137204 (2013)

[4] S. Miyahara and K. Ueda, Theory of the orthogonal dimer heisenberg spin model for SrCu$_2$(BO$_3$)$_2$, J. Phys. Condens. Matter 15, R327 (2003)

[5] B. Sriman Shastry and B. Sutherland, Exact ground state of a quantum mechanical antiferromagnet, Physica B+C 108, 1069 (1981)

[6] S. Miyahara and K. Ueda, Exact dimer ground state of the two dimensional heisenberg spin system SrCu$_2$(BO$_3$)$_2$, Phys. Rev. Lett. 82, 3701 (1999)

[7] J. L. Jiménez, S. F. G. Crone, E. Fogh, M. E. Zayed, R. Lortz, E. Pomjakushina, K. Conder, A. M. Läuchli, L. Weber, S. Wessel, A. Honecker, B. Normand, C. Rüegg, P. Corboz, H. M. Rennow, and F. Mila, A magnetic molecular analogue to the critical point of water, Nature 592, 370 (2021)

[8] A. Koga and N. Kawakami, Quantum phase transitions in the Shastry-Sutherland model for SrCu$_2$(BO$_3$)$_2$, Phys. Rev. Lett. 84, 4461 (2000)

[9] P. Corboz and F. Mila, Tensor network study of the Shastry-Sutherland model in zero magnetic field, Phys. Rev. B 87, 115144 (2013)

[10] M. E. Zayed, C. Rüegg, J. Larrea J., A. M. Läuchli, C. Panagopoulos, S. S. Saxena, M. Ellerby, D. F. McMorrow, T. Strässle, S. Klotz, G. Hamel, R. A. Sadykov, V. Pomjakushin, M. Boehm, M. Jiménez-Ruiz, A. Schneidewind, E. Pomjakushina, M. Stingaciu, K. Conder, and H. M. Rennow, 4-spin plaquette singlet state in the shastry–sutherland compound SrCu$_2$(BO$_3$)$_2$, Nat. Phys. 13, 962 (2017)

[11] S. Haravifard, D. Graf, A. E. Feiguin, C. D. Batista, J. C. Lang, D. M. Silevitch, G. Srajer, B. D. Gaulin, H. A. Dabbekowsa, and T. F. Rosenbaum, Crystallization of spin superlattices with pressure and field in the layered magnet SrCu$_2$(BO$_3$)$_2$, Nat. Commun. 7, 11956 (2016)

[12] Z. Shi, S. Dissanayake, P. Corboz, W. Steinhardt, D. Graf, D. M. Silevitch, H. A. Dabbekowsa, T. F. Rosenbaum, F. Mila, and S. Haravifard, Discovery of quantum phases in the Shastry-Sutherland compound SrCu$_2$(BO$_3$)$_2$ under extreme conditions of field and pressure, Nat Commun. 13, 2301 (2022)

[13] T. Sakurai, Y. Hirao, K. Hijii, S. Okubo, H. Ohta, Y. Uwatoko, K. Kudo, and Y. Koike, Direct Observation of the Quantum Phase Transition of SrCu$_2$(BO$_3$)$_2$ by High-Pressure and Terahertz Electron Spin Resonance, J. Phys. Soc. Jpn. 87, 033701 (2018)

[14] J. Guo, G. Sun, B. Zhao, L. Wang, W. Hong, V. A. Sidorov, N. Ma, Q. Wu, S. Li, Z. Y. Meng, A. W. Sandvik, and L. Sun, Quantum Phases of SrCu$_2$(BO$_3$)$_2$ from High-Pressure Thermodynamics, Phys. Rev. Lett. 124, 206602 (2020)

[15] G. Randri, A. Saul, H. A. Dabbekowsa, M. B. Salamon, and M. Jaime, Magnetic nanopointograph in the SrCu$_2$(BO$_3$)$_2$ Shastry-Sutherland lattice, Proc. Natl. Acad. Sci. 112, 1971 (2015)

[16] Y. Narumi, N. Terada, Y. Tanaka, M. Iwaki, K. Katsumata, K. Kindo, H. Kageyama, Y. Ueda, H. Toyokawa, T. Ishikawa, and H. Kitamura, Field induced lattice deformation in the quantum antiferromagnet SrCu$_2$(BO$_3$)$_2$, J. Phys. Soc. Jpn. 78, 043702 (2009)

[17] M. Jaime, R. Daou, S. A. Crooker, F. Weickert, A. Uchida, A. E. Feiguin, C. D. Batista, H. A. Dabbekowsa, and B. D. Gaulin, Magnetostricition and magnetic texture to 100.75 tesla in frustrated SrCu$_2$(BO$_3$)$_2$, Proc. Natl. Acad. Sci. 109, 12404 (2012)

[18] S. E. Sebastian, N. Harrison, P. Sengupta, C. D. Batista, S. Francisco, E. Palm, T. Murphy, N. Marcano, H. A. Dabbekowsa, and B. D. Gaulin, Fractализation drives crystalline states in a frustrated spin system, Proc. Natl. Acad. Sci. 105, 20157 (2008)

[19] F. Levy, I. Sheikin, C. Berthier, M. Horvatić, M. Taki-gawa, H. Kageyama, T. Waki, and Y. Ueda, Field dependence of the quantum ground state in the Shastry-Sutherland system SrCu$_2$(BO$_3$)$_2$, EPL (Europhysics Letters) 81, 67004 (2008)

[20] K. Kodama, M. Takigawa, M. Horvatić, C. Berthier, H. Kageyama, Y. Ueda, S. Miyahara, F. Becca, and F. Mila, Magnetic superstructure in the two-dimensional quantum antiferromagnet SrCu$_2$(BO$_3$)$_2$, Science 298, 295 (2002)

[21] M. Takigawa, M. Horvatić, T. Waki, S. Krämer, C. Berthier, F. Lévy-Bertrand, I. Sheikin, H. Kageyama, Y. Ueda, and F. Mila, Incomplete devil’s staircase in the magnetization curve of SrCu$_2$(BO$_3$)$_2$, Phys. Rev. Lett. 110, 067210 (2013)

[22] M. Takigawa, T. Waki, M. Horvatić, and C. Berthier, Novel ordered phases in the orthogonal dimer spin system SrCu$_2$(BO$_3$)$_2$, J. Phys. Soc. Jpn. 79, 014705 (2010)

[23] C. Knetter, A. Bühler, E. Müller-Hartmann, and G. S. Uhrig, Dispersion and symmetry of bound states in the Shastry-Sutherland model, Phys. Rev. Lett. 85, 3958 (2000)

[24] T. Momoi and K. Totsuka, Magnetization plateaus as insulator-superfluid transitions in quantum spin systems, Phys. Rev. B 61, 3231 (2000)

[25] T. Momoi and K. Totsuka, Magnetization plateaus of the Shastry-Sutherland model for SrCu$_2$(BO$_3$)$_2$: Spin-density wave, supersolid, and bound states, Phys. Rev. B 62, 15067 (2000)

[26] Y. Fukumoto, Magnetization plateaus in the Shastry-Sutherland model for SrCu$_2$(BO$_3$)$_2$: Results of fourth-order perturbation expansion with a low-density approximation, J. Phys. Soc. Jpn. 70, 1397 (2001)

[27] S. Takeyama, R. Sakakura, Y. H. Matsuda, A. Miyata, and M. Tokunaga, Precise magnetization measurements by parallel self-compensated induction coils in a vertical single-turn coil up to 103 T, J. Phys. Soc. Jpn. 81, 014702 (2012)

[28] S. Zherlitsyn, S. Schmidt, B. Wolf, H. Schwenk, B. Lüthi, H. Kageyama, K. Onizuka, Y. Ueda, and K. Ueda, Sound-wave anomalies in SrCu$_2$(BO$_3$)$_2$, Phys. Rev. B 62, R6967 (2000)

[29] B. Wolf, S. Zherlitsyn, S. Schmidt, B. Lüthi, H. Kageyama, and Y. Ueda, Soft acoustic modes in the two-dimensional spin system SrCu$_2$(BO$_3$)$_2$, Phys. Rev. Lett. 86, 4847 (2001)

[30] S. Imajo, N. Matsuyama, T. Nomura, T. Kihara, S. Nakamura, C. Marcenat, T. Klein, G. Seyfarth, C. Zhong,
H. Kageyama, K. Kindo, T. Momoi, and Y. Kohama, Magnetically hidden state on the ground floor of the magnetic devil’s staircase, arXiv:2203.07607 (2022).

B. Lüthi, Physical Acoustics in the Solid State (Springer, 2005).

F. Verstraete and J. I. Cirac, Renormalization algorithms for Quantum-Many Body Systems in two and higher dimensions, arXiv:cond-mat/0407066 (2004).

Y. Nishio, N. Maeshima, A. Gendiar, and T. Nishino, Tensor Product Variational Formulation for Quantum Systems, Preprint (2004), arXiv:cond-mat/0401115.

J. Jordan, R. Orús, G. Vidal, F. Verstraete, and J. I. Cirac, Classical Simulation of Infinite-Size Quantum Lattice Systems in Two Spatial Dimensions, Phys. Rev. Lett. 101, 250602 (2008).

N. Miura, T. Osada, and S. Takeyama, Research in super-high pulsed magnetic fields at the megagauss laboratory of the university of Tokyo, J. Low Temp. Phys. 133, 139 (2003).

H. Kageyama, K. Onizuka, T. Yamauchi, and Y. Ueda, Crystal growth of the two-dimensional spin gap system SrCu2(BO3)2, Journal of Crystal Growth 206, 65 (1999).

T. Nomura, A. Hauspurg, D. I. Gorbunov, A. Miyata, E. Schulze, S. A. Zvyagin, V. Tsurkan, Y. H. Matsuda, Y. Kohama, and S. Zherlitsyn, Ultrasound measurement technique for the single-turn-coil magnets, Rev. Sci. Instrum. 92, 063902 (2021).

S. Zherlitsyn, B. Wustmann, T. Herrmannsdörfer, and J. Wośnitzka, Magnet-technology development at the dresden high magnetic field laboratory, J. Low Temp. Phys. 170, 447 (2013).

A. Ikeda, T. Nomura, Y. H. Matsuda, S. Tani, Y. Kobayashi, H. Watanabe, and K. Sato, High-speed 100 MHz strain monitor using fiber bragg grating and optical filter for magnetostriiction measurements under ultrahigh magnetic fields, Rev. Sci. Instrum. 88, 083906 (2017).

A. Ikeda, Y. H. Matsuda, and K. Sato, Two spin-state crystallizations in LaCoO3, Phys. Rev. Lett. 125, 177202 (2020).

R. Schönemann, G. Rodriguez, D. Rickel, F. Balakirev, R. D. McDonald, J. A. Evans, B. Maiorov, C. Paillard, L. Bellaiche, A. V. Stier, M. B. Salamon, K. Gofryk, and M. Jaime, Magnetoelastic standing waves induced in UO2 by microsecond magnetic field pulses, Proc. Natl. Acad. Sci. 118, e211055118 (2021).

Supplemental materials including the raw data of the experimental results and discussions on the derivatives of the free energy are available at http://.

P. Corboz and F. Mila, Crystals of bound states in the Shastry-Sutherland model, Phys. Rev. Lett. 112, 147203 (2014).

H. C. Jiang, Z. Y. Weng, and T. Xiang, Accurate Determination of Tensor Network State of Quantum Lattice Models in Two Dimensions, Phys. Rev. Lett. 101, 090603 (2008).

L. Wang and F. Verstraete, Cluster update for tensor network states, arXiv:1110.4362 (2011).

P. Corboz, S. R. White, G. Vidal, and M. Troyer, Stripes in the two-dimensional $t-J$ model with infinite projected entangled-pair states, Phys. Rev. B 84, 041108 (2011).

P. Corboz, T. M. Rice, and M. Troyer, Competing States in the $t-J$ Model: Uniform d-Wave State versus Stripe State, Phys. Rev. Lett. 113, 046402 (2014).

T. Nishino and K. Okunishi, Corner Transfer Matrix Renormalization Group Method, J. Phys. Soc. Jpn. 65, 891 (1996).

R. Orús and G. Vidal, Simulation of two-dimensional quantum systems on an infinite lattice revisited: Corner transfer matrix for tensor contraction, Phys. Rev. B 80, 094403 (2009).

P. Corboz, R. Orus, B. Bauer, and G. Vidal, Simulation of strongly correlated fermions in two spatial dimensions with fermionic projected entangled-pair states, Phys. Rev. B 81, 165104 (2010).

P. Corboz and F. Mila, Tensor network study of the Shastry-Sutherland model in zero magnetic field, Phys. Rev. B 87, 115144 (2013).

H. N. Phien, J. A. Bengua, H. D. Tuan, P. Corboz, and R. Orus, Infinite projected entangled pair states algorithm improved: Fast full update and gauge fixing, Phys. Rev. B 92, 035142 (2015).

S. Miyahara and K. Ueda, Thermodynamic properties of the three-dimensional orthogonal dimer model for SrCu2(BO3)2, J. Phys. Soc. Jpn. 69 Suppl. B, 72 (2000).

A. Zorko, D. Arcon, H. van Tol, L. C. Bruzel, and H. Kageyama, X-band ESR determination of Dzyaloshinsky-Moriya interaction in the two-dimensional SrCu2(BO3)2 system, Phys. Rev. B 69, 174420 (2004).

S. Miyahara, F. Becca, and F. Mila, Theory of spin-density profile and lattice distortion in the magnetization plateaus of SrCu2(BO3)2, Phys. Rev. B 68, 024401 (2003).

K. Momma and F. Izumi, VESTA: a three-dimensional visualization system for electronic and structural analysis, J. Appl. Crystallogr. 41, 653 (2008).
VIII. EXPERIMENTAL DETAILS

In this study, we used two types of pulsed magnets, the single-turn coil (STC) in the ISSP, University of Tokyo and the dual-coil pulsed magnet at the HLD in Dresden. Figure S1 shows the typical waveforms of these magnets. The STC is a semi-destructive technique where the field duration is limited to several µs. Because of this limitation, special experimental efforts are needed to measure the properties of materials in STC experiments. In this section, we discuss the experimental technique and present some further results.

For studying the ultrasonic properties up to 150 T, we used the continuous-wave (CW) excitation technique [37]. The experimental setting [Fig. S2(a)] is very similar with the conventional pulse-echo technique, where the sample is sandwiched by two LiNbO₃ transducers. In the CW technique, the transducer is excited continuously without pulse modulation. Therefore, the ultrasound signal is also continuously detected even in the µs timescale. However, the detected signal includes cross-talk and many reflections, which affects the phase and amplitude of the acoustic waves. As discussed in Ref. [37], this effect becomes negligibly small if the sample length and shape are optimized. The relative change of the sound velocity ∆v/v₀ is proportional to the relative change of the phase ∆Φ/Φ₀ as

$$\frac{\Delta v}{v_0} = -\frac{\Delta \Phi}{\Phi_0} = -\frac{\Delta \Phi}{2\pi f \tau_0},$$

(2)

where f and τ₀ are the ultrasound frequency and the time delay of the ultrasound for a single transmitted signal.

In this study, we first tested the installation up to 40 T in the STC and confirmed that the obtained data are consistent with the pulse-echo results. Here, we used the sample length of 1.1 mm, with which the time delay of the ultrasound is reasonably small.

Figure S1 shows the raw ultrasound data up to 125 T obtained at 3.2 K. The magnetic field profile is shifted by taking into account the propagation time of the ultrasound [from blue to black in Fig. S3(a)]. The detected signal is shown in Fig. S3(b). By applying the numerical lock-in, the phase shift (ΔΦ) and amplitude of the signal are extracted as shown in Fig. S3(c) and Fig. S3(d), respectively. Anomalies related to the phase transitions are observed both in the field-up and field-down sweeps. Note, that the detected phase has always ±2π ambiguity. It means that if the phase change is very large and fast, the correct phase shift might be overlooked. This might be specifically the case at the 2/5-1/2 plateau region (∼ 80 T, highlighted by light green), where the sound velocity changes by −40% per 5 T. Such a drastic sound velocity change is very challenging to follow in the STC experiment, because the sound velocity changes significantly within the sound propagation time even for 1.1 mm sample. Therefore, we rely on the results obtained in the non-destructive pulsed magnet by the conventional pulse-echo technique, and shifted accordingly the STC results in this field range [Fig. S3(c)].

For studying the magnetostriction, we used the fiber-Bragg grating (FBG) [39]. The schematic setting is shown in Fig. S2(b). The FBG is fixed to the sample, and the sample deformation is monitored by the wavelength of the reflected light. By using the optical filter, the wavelength shift is detected as the amplitude change...
Fig. S 3. Raw data of the ultrasound experiment for the \( c_{66} \) mode at 3.2 K up to 125 T. (a) Magnetic-field profile. The black curve is shifted from the original profile (blue) by taking into account the ultrasound-propagation time. (b) Detected ultrasound signal. (c) Phase change and (d) amplitude of the detected signal. The exact phase change is challenging to extract in the regions highlighted by light green because of the rapid change of the sound velocity in a very narrow magnetic field range.

of the reflected light (for detail, see Ref. [39]). With this technique, the sample length change can be optically detected, which is a great advantage in the STC experiments. The biggest challenge performing the FBG measurement with STC is the sample vibration [40, 41]. When a magneto-structural phase transition occurs, a slight lattice deformation triggers a vibration of a crystal. When the sample shape is regular with parallel surfaces, this vibration results in the resonant oscillation of the crystal. Such oscillations lead to a periodic noise with the resonant frequency determined by the sample dimensions and the sound velocity. To attenuate such oscillations, we used (i) the sample with irregular shape and (ii) grease covering the whole sample [Fig. S2(c)]. To weaken the resonant oscillation, the quality factor of the resonance has to be reduced. In this study, we used the crystal with one polished surface, but without any parallel surfaces. For such crystal, the phases of the reflected acoustic waves are random, and the resonant oscillations are strongly damped. Additionally, with vacuum grease, the sample is mechanically coupled with the sample stage. In this case, the quality factor of the resonance is strongly reduced by the mass-loading effect, and the resonant frequency becomes much lower than the STC characteristic frequency. Figure S4 shows the results of the magnetostriction experiment with and without vacuum grease. The resonant oscillations are strongly damped by the grease, although the size of the anomaly is also reduced. Therefore, in this study, we do not discuss the magnitude of the magnetostriction and only focus on the critical fields. The anomalies at \( H_{c6} \) and \( H_{c7} \) are well reproduced for the field-up and field-down sweeps.

Figure S5 summarizes the maximum-field dependence of the results. Figure S5(a) shows the phase of the ultrasound signal of the \( c_{66} \) mode. As discussed, the rapid change of the sound velocity is challenging to capture by this technique, which is the case in the region highlighted by light green and blue. Nevertheless, the overall features of the sound velocity are well reproduced; the softening in the 1/4 plateau, the hardening in the 1/3 plateau, the softening towards the 1/2 plateau, the constant velocity up to \( H_{c7} = 116 \) T, and the slope change around \( H_{c8} = 127 \) T. Figure S5(b) shows the magnetostriction measured for a single FBG setting, which survives even after the STC experiments. The slight difference might be due to the covering conditions with vacuum grease, which melts each time after the experiment. Again, the overall features are well reproduced; the rapid decrease at 80 T, the increase at \( H_{c6} = 108 \) T, the maximum at \( H_{c7} = 116 \) T, and the kink at \( H_{c8} = 127 \) T. The anomaly at \( H_{c9} = 139 \) T, which corresponds to the saturation of magnetization, is also reproduced for the ultrasound and magnetostriction measurements.

Fig. S 4. Raw magnetostriction data (\( \Delta L_{c} \)) at 4.2 K up to 122 T. Reflected light intensity (left) and magnetic field (right, blue curve) are plotted as a function of time. The results with and without grease are compared. The results (black curve) are averaged with the time window of 40 ns.
IX. MAGNETIC CONTRIBUTIONS TO THE $c_{66}$ MODE

In this section, we discuss the relation between the first and the second derivatives of the magnetic energy with respect to the displacement $\varepsilon$ associated with the mode probed by $c_{66}$. Without the magnetic contribution, and up to a constant, the structural energy is minimal for $\varepsilon = 0$, and its expansion in $\varepsilon$ reads:

$$E_{\text{struc}} = b\varepsilon^2 + c\varepsilon^3$$

where $b$ describes the harmonic potential and $c$ the cubic anharmonic contribution.

As shown by iPEPS calculations, the magnetic contribution to the energy has both linear and quadratic contributions:

$$E_{\text{mag}} = a\varepsilon + b'\varepsilon^2$$

with $a = dE_{\text{mag}}/d\varepsilon$ and $b' = (1/2)d^2E_{\text{mag}}/d\varepsilon^2$.

Because of the linear term of $E_{\text{mag}}$, the minimum of the total energy $E_{\text{tot}} = E_{\text{struc}} + E_{\text{mag}}$ occurs at a non-zero value $\varepsilon_0$ which is solution of the equation

$$\frac{dE_{\text{tot}}}{d\varepsilon} = a + 2(b + b')\varepsilon + 3c\varepsilon^2 = 0.$$ 

If $\varepsilon_0$ is very small, which will be the case if $a, c \ll b$, then it is given by

$$\varepsilon_0 \simeq -\frac{a}{2(b + b')}.$$ 

Now let us expand the total energy around the new minimum by setting $\varepsilon = \varepsilon_0 + \delta$. Up to the second order in $\delta$, we get:

$$E_{\text{tot}}(\delta) = a\varepsilon_0 + (b + b')\varepsilon_0^2 + \frac{3c}{2(b + b')}\varepsilon_0^3$$

$$+ (a + 2(b + b')\varepsilon_0 + 3c\varepsilon_0^2)\delta$$

$$+ (b + b' + 3c\varepsilon_0)\delta^2.$$ 

The coefficient of the linear term vanishes because of the condition satisfied by $\varepsilon_0$, and, in the limit of small $\varepsilon_0$, the coefficient of the quadratic term is given by

$$b + b' = \frac{3c}{2(b + b')}a.$$ 

As anticipated, it contains a contribution proportional to $b'$, hence to $d^2E_{\text{mag}}/d\varepsilon^2$, and a contribution proportional to $a$, hence to $dE_{\text{mag}}/d\varepsilon$. The contribution of the first derivative comes from the anharmonicity - its coefficient is proportional to $c$. 

Fig. S 5. (a) Phase shift of the acoustic wave for the $c_{66}$ mode at 3.2 K and (b) magnetostriction along the c axis at 4.2 K measured to various maximum fields in the STC. The curves are deliberately shifted along the vertical axis for clarity. It is very challenging to reconstruct correctly the phase change in the green and blue area because very large and fast changes in the sound velocity in this magnetic field region.