Magnetic nanopantograph in the SrCu$_2$(BO$_3$)$_2$ Shastry-Sutherland lattice

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Magnetic materials having competing, i.e., frustrated, interactions can display magnetism prolific in intricate structures, discrete jumps, plateaus, and exotic spin states with increasing applied magnetic fields. When the associated elastic energy cost is not too expensive, this high potential can be enhanced by the existence of an omnipresent magnetoelastic coupling. Here we report experimental and theoretical evidence of a nonnegligible magnetoelastic coupling in one of these fascinating materials, SrCu₂(BO₃)₂ (SCBO). First, using pulsed-field transversal and longitudinal magnetostriction measurements we show that its physical dimensions, indeed, mimic closely its unusually rich field-induced magnetism. Second, using density functional-based calculations we find that the driving force behind the magnetoelastic coupling is the CuOCu superexchange angle that, due to the orthogonal Cu²⁺ dimers acting as pantographs, can shrink significantly (0.44%) with minute (0.01%) variations in the lattice parameters. With this original approach we also find a reduction of ~10% in the intradimer exchange integral J, enough to make predictions for the highly magnetized states and the effects of applied pressure on SCBO.

magnetostriction | high magnetic fields | spin-lattice coupling | density functional theory | Shastry–Sutherland

It has long been understood that magnetoelastic coupling can move magnetic materials phase boundaries in temperature and field and even change the order and/or universality class of magnetic transitions (1). Model Hamiltonians with effective exchange interactions are the common theoretical tool to tackle the complex behaviors of quantum magnet systems (2) and, indeed, these effective exchange interactions depend on subtleties of the electronic structure that, in turn, are naturally linked to the structural degrees of freedom of the system. When magnetoelastic effects are present, structural changes can also modify the macroscopic magnetic state via changes in the effective parameters of the model Hamiltonian. Simply posed, it is challenging to interpret experimental results at a point of high interest in a predicted (H,T) phase diagram of a magnetic material under consideration for fundamental studies or applications without knowing the effects that unavoidable lattice changes have in the exchange interactions as we drive our system toward such a point. Hence, it is highly desirable to be able to quantify such lattice effects.

SrCu₂(BO₃)₂ (SCBO) is an especially fascinating example of a low-dimension, frustrated quantum antiferromagnetic system. It crystallizes in a tetragonal structure (3) in which layers of [CuBO₃]⁻ (Fig. L1) are stacked along the c axis and separated by planes of Sr²⁺ ions (Fig. LB). The magnetically active Cu²⁺ ions form a 2D arrangement of mutually orthogonal dimers (Fig. L4). The magnetic properties of this compound can be closely described through a 2D Heisenberg Hamiltonian (4):

\[ H = J \sum_{\text{nn}} \mathbf{S}_i \cdot \mathbf{S}_j + J' \sum_{\text{nnn}} \mathbf{S}_i \cdot \mathbf{S}_j, \]  

where \( J \) and \( J' \) are respectively the nearest-neighbor (intradimer) and next-nearest-neighbor (interdimer) exchange integrals in the [CuBO₃]⁻ planes. Although \( J \) and \( J' \) are both positive, leading to frustrated antiferromagnetic (AFM) interactions, Shastry and Sutherland (5) have shown the remarkable property that the Hamiltonian (Eq. 1) admits the direct product of dimer singlet states as an exact eigenstate. It has been first shown that this spin gap can be closed [the spin gap never s = 0 wavefunction is the ground state for \( J' / J \leq 0.7 \), separated from the first excited state by a spin gap (4, 6, 7]. More recently, the critical value has been refined to be \( \approx 0.675 \) (8–10). The spin gap can be closed [the spin gap never strictly closes, as Dzyaloshinsky–Moriya terms cause mixing of spin-triplet and spin-singlet states (11)], and cascading magnetic states can be induced, by magnetic fields exceeding \( \approx 20 \) T (12).

The first indications of a significant lattice involvement in this system were evidenced in the sound velocity measurements by Wolf et al. (13), subsequently studied using X-ray diffraction at low temperature and under high magnetic field by Narumi et al. (14). These were followed by neutron diffraction experiments carried out by Vecchini et al. (15) and Haravifard et al. (16). In the former, structural changes due to the thermal excitation of the magnetic degrees of freedom were directly measured. In the latter the increased lifetime (inelastic linewidths) in a subset of the acoustic phonons has been shown to correlate with the

Significance

The spins of the unpaired electrons in a solid tend to align along an applied magnetic field. In the case of antiferromagnetic materials having competing interactions (frustration) it is common to observe that the magnetization increases, exhibiting complicated structures with discrete jumps and plateaus. SrCu₂(BO₃)₂ is one of these materials, for which we find experimentally that its macroscopic physical dimensions also change with the magnetic field, mimicking the behavior in the magnetization. Using quantum mechanics, we show quantitatively that due to the orthogonal arrangement of the magnetic Cu²⁺ dimers acting as pantographs, minute deformations allow significant reduction in the effective interactions responsible for the antiferromagnetism. This drop is sufficient to compensate the elastic energy loss in the lattice deformation.

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formation of the singlet ground state near 10 K in zero field. In a recent study, Jaime et al. (17) performed magnetostriction experiments to 100 T, showing that the crystallographic $c$ axis is an extraordinarily sensitive witness to the magnetic structure and superstructure. However sensitive, the $c$-axis results do not allow for a direct examination of the spin-lattice correlations within the Cu-dimer planes (Fig. 1A).

**Experimental Results**

Using an experimental setup modified from one previously discussed (17), where an optical fiber Bragg grating (FBG) sensor is placed perpendicular to the applied magnetic field, we obtained the first high-resolution (better than $10^{-6}$) in-plane magnetostriction at $T = 1.36$ K (Fig. 2). In our experiment we observe a contraction of the $a$ axis that is sensitive to, and shows features at, the magnetic fields identified as onset of the 1/8, 1/4, and 1/3 magnetization plateaus and a concomitant expansion of the $c$ axis with an FBG sensor in the conventional configuration parallel to the applied field. Our new data are consistent with $a$-axis vs. field data from Narumi et al. (14), although the X-ray experiment did not resolve individual plateaus. The observed $\Delta a/a = -1.4 \times 10^{-4}$ and $\Delta c/c = 1.15 \times 10^{-4}$ put the relative change in volume at $\Delta V/V = -1.65 \times 10^{-4}$ for the 1/3 plateau.

**Model**

From a magnetic point of view, one can expect that the system will respond to the external magnetic field by modifying the internal coordinates of ions playing a role in the magnetic interactions. The modification of any other internal coordinates would have an elastic energy cost without magnetic energy gain. As already pointed out (14, 15), the main internal parameter related with the magnetic properties in this compound is the CuOCu superexchange angle ($\alpha$) mediating the intradimer superexchange interaction. This angle is, indeed, expected to decrease toward 90° with the applied magnetic field as this distortion would weaken the AFM superexchange interaction (18–21) through a reduction of the Cu-3d/O-2p hopping.

The orthogonal arrangement of the dimers in SCBO allows for a variation of the angle with a minimum lattice deformation. This double-pantograph (22) effect can be most easily visualized in Fig. 3 by considering the atoms moving as sketched. Each pantograph magnifies the decrease of the internal superexchange angles, but the two do not substantially change the overall length.

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of the array. This argument can be demonstrated in a more rigorous way. Indeed, neglecting the buckling, the tetragonal unit cell parameter and the angle can be written as follows in terms of interatomic distances in the [CuBO$_3$]$^-$ layer (Fig. 3):

$$a \approx \frac{1}{\sqrt{2}} [d_{O-O} + 2d_{O-B} + 2d_{B-Cu} + d_{Cu-Cu}]$$

and

$$\tan \frac{\alpha}{2} \approx \frac{d_{Cu-Cu}}{d_{O-O}}.$$ 

Assuming that the O–B and B–Cu bonds are not affected by the magnetic field, and calling $x$ the O–O and $y$ the Cu–Cu distances, their variations can be written as

$$\Delta a = \frac{1}{\sqrt{2}} (\Delta x + \Delta y)$$

and

$$\Delta \alpha = \frac{2}{x^2 + y^2} \left[ \frac{\Delta y}{y} - \frac{\Delta x}{x} \right].$$

Under an increasing magnetic field, the system can reduce the magnetic contribution to the total energy by decreasing the superexchange angle ($\Delta \alpha < 0$) through an increase of the O–O distance ($\Delta x > 0$) or a decrease of the Cu–Cu one ($\Delta y < 0$). Because the variation in the Cu–Cu distance compensates the variation in the O–O distance $\Delta x \approx -\Delta y$, it follows that $\Delta \alpha / a \ll \Delta \alpha$. The magnetic energy gain from the increase in antiferromagnetic exchange is not, therefore, at the expense of a significant increase in lattice energy.

**Theoretical Results**

**Structure Relaxation—Angle.** To gain insight into the modification of the internal structural parameters and their consequences on the electronic structure and magnetic interactions with a change of the magnetic order, total energy calculations have been performed with the Quantum Espresso (23) code.

As, in our problem, magnetostriction involves only very weak structural variations, it would be of interest to compare the structural relaxation of two extreme magnetic states, namely the ground state configuration (a product of dimer singlets) and the ferromagnetic (FM) state expected at saturation. Unfortunately, the ground state solution cannot be written as a single Kohn–Sham determinant and is therefore not accessible with state-of-the-art density functional theory (DFT) codes for periodic systems. For this reason, we have optimized the lattice parameters and internal atomic coordinates of a Néel-like AFM ordered structure and of the FM state (Fig. 1 C–F). Using the Quantum Espresso code (23), we obtained lattice parameters ($a = 9.123$ Å and $c = 6.853$ Å) that are slightly overestimated as is usually the case with the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) functional. As expected from the above discussion, due to the $(\Delta \tau, \Delta \nu)$ compensation effect, no measurable difference between the lattice parameters of the AFM and FM ordered structures was found. The order of magnitude of their relative difference (experimentally found to be $\approx 10^{-4}$) indeed falls within the limit of accuracy of DFT when trying to calculate the structural changes between two magnetic orders with different space symmetries.

The difference in $a$ and the O–O and Cu–Cu distances (respectively $x$ and $y$) between the two magnetic structures are more easy to assess with DFT. A variation of the angle of $\alpha = -0.43^\circ$ ($98.13^\circ$ and $97.70^\circ$ for the AFM and FM structures, respectively) has been found whereas the O–O and Cu–Cu distance changes are $\Delta r = 0.011$ Å and $\Delta y = 0.009$ Å, respectively. As already mentioned, their relative variations ($\Delta r/\alpha \approx 44 \times 10^{-4}$ and $\Delta y/\nu \approx -31 \times 10^{-4}$) are larger than the variation of $\Delta \alpha / a$.

**Effective Exchange Interactions from Energy Differences.** The computation of magnetic couplings was first carried out within the broken symmetry formalism, i.e., by mapping total energies corresponding to various collinear spin arrangements within a supercell onto a Heisenberg Hamiltonian,

$$H = H_0 + \sum_{i<j} J_{ij} S_i \cdot S_j,$$

where $H_0$ is the spin-independent part of the Hamiltonian, $J_{ij}$ are the magnetic couplings to determine, and $S_i$ and $S_j$ are, in our case, the $S = 1/2$ spin operators localized on Cu$^{2+}$ ions located at sites $i$ and $j$, respectively. It is straightforward to show that the expectation value of the Hamiltonian (6) on a DFT state $|\alpha\rangle$ (obtained by preparing the initial electron density according to
a particular collinear spin arrangement in the supercell and performing a self-consistent calculation until convergence) can be simply written under the form of an Ising Hamiltonian 

\[ e_{\alpha}^{\text{DFT}} = \langle \alpha | \hat{H} | \alpha \rangle = e_0 + \frac{1}{4} \sum_{i,j} J_{ij} \sigma_i \sigma_j \]  

with \( \sigma_i = \pm 1 \). It is important to note that this broken symmetry procedure preserves the quantum nature of the problem. In strongly localized systems, such as 3d transition metal oxides, Eq. 7 can be used to model a large set of spin configurations. A numerical evaluation of the couplings is thus obtained through a least-squares minimization of the difference between DFT and Ising relative energies of the set of spin configurations (25–27).

In the case of SCBO the determination of the magnetic couplings up to the fifth nearest neighbor (in the 3D lattice) can be performed using a 44-atom tetragonal cell. Taking crystal and spin reversal symmetries into account, this leads to a total of 22 distinct spin configurations. The calculations using the internal parameters of the relaxed AFM and FM ordered structures give \( J = 157 \) K and \( J = 138 \) K, respectively. A reduction of the in-plane nearest-neighbor interaction of \( \sim -12\% \) is therefore obtained, in agreement with the decrease of the angle. On the contrary, the in-plane second-nearest-neighbor interaction remains the same \( J' = 71 \) K in both cases. Additional calculated couplings correspond to interplanar couplings. They are all antiferromagnetic and show a much weaker amplitude \((\pm 4)\), independent of the set of internal coordinates employed in the calculations. The results of the mapping procedure are shown in Fig. 4.

**Effective Exchange Interactions from Band Structure–Wannier Functions.** An alternative evaluation of the AFM contribution to the magnetic couplings can be achieved through a mapping of the paramagnetic band structure onto a single-band Hubbard model at half filling, which eventually reduces to an Heisenberg model in the strongly correlated limit. In this framework, the effective antiferromagnetic interaction is given by \( J_{\text{AFM}} = 4d^2/U \).

The Wannier-interpolated band structure obtained following this procedure is superimposed to the GGA-PBE band structure in Fig. 5. Fig. 5, Inset shows the maximally localized Wannier functions (MLWF) calculated for the FM internal coordinates. Besides the central Cu-\( d_{\alpha} \) component, large antibonding tails of O-2p character mediating the dominant in-plane superexchange antiferromagnetic interactions are also clearly visible. Note that a MLWF calculated for the AFM internal coordinates would be indistinguishable at this scale. The hopping integrals \( t \) and \( t' \) corresponding to the first and second effective exchange interactions are 0.153 eV and \(-0.096\) eV for the AFM internal coordinates and 0.148 eV and \(-0.096\) eV for the FM ones.

There is a small but measurable decrease of the nearest-neighbors hopping interaction \( t \) but no difference in the next-nearest-neighbors interaction \( t' \). The different behavior can be ascribed to the decrease of the intradimer CuOCu superexchange angle contrasting with the above mentioned rigidity of the BO4 group. The variation of the nearest-neighbors effective exchange interaction estimated through this approach is \( \Delta J_{\text{AFM}}/J_{\text{AFM}} = -6.5\% \), i.e., of the same order of magnitude as the modification estimated with the broken symmetry formalism. The difference is likely to arise from the fact that this procedure gives only the antiferromagnetic contribution to the total effective exchange interaction missing a known nonnegligible ferromagnetic component (28).

**Discussion**

It is possible to establish a relation between the intradimer CuOCu superexchange angle and the subsequent lattice parameter variations based on a simple geometrical interpretation of the structural data available on this compound. We should first eliminate \( \Delta x \) in Eqs. 4 and 5 to obtain

\[ \Delta y = \frac{2(x+y)}{x^2+y^2} \Delta y - \frac{2\sqrt{2}y}{x^2+y^2} \Delta a. \]

To further eliminate \( \Delta y \), we can consider that the structural variations induced by thermal excitation of the dimer singlets are equivalent to the variations obtained by application of an external magnetic field. Under this assumption, a linear dependence \( \Delta a = k \Delta y \) with \( k = 36.6 \pm 0.8 \) Å\(^{-1} \) = 0.64 ± 0.01 Å\(^{-1} \) (Fig. S1) can be deduced from temperature-dependent neutron diffraction experiments (15) to obtain

\[ \Delta a = \frac{2\sqrt{2}y}{2(x+y) - k(x^2+y^2)} \Delta a. \]

Similar functions of \( x, y, \) and \( k \) can be obtained for \( \Delta x, \Delta y, \) and \( \Delta d \) the Cu–O distance (SI Text). Finally, replacing \( x, y, \) and \( a \) by their experimental values (15), we obtain

\[ \Delta a \approx 35 \Delta a, \quad \Delta x / x \approx -17 \Delta a / a, \quad \Delta y / y \approx 19 \Delta a / a, \quad \Delta d / d \approx -26 \times 10^{-2}. \]

showing that the deformation of the lattice parameter can be related to one order of magnitude larger variations of the internal parameters. Indeed, the experimentally measured low temperature magnetostriiction at 60 T is \( 1.15 \times 10^{-4} \) and \(-1.4 \times 10^{-4} \) along the \( c \) and \( a \) axes, respectively. These changes imply a drop in \( a \) of 0.28\% and relative variations \( \Delta x / x \approx 24 \times 10^{-4} \) and \( \Delta y / y \approx -26 \times 10^{-4} \). Furthermore, one should expect that magnetostriiction to 100 T along the \( c \) axis of 1.6 \times 10^{-4} (17) would be accompanied by magnetostriiction of 1.95 \times 10^{-4} along the \( a \) axis and a change in \( a \) of 0.4\%, altogether in remarkable agreement with our DFT results, confirming that \( a \) is the driving mechanism behind the magnetoelastic coupling in SCBO.

Coming back to DFT calculations, we can now confirm that the energetic arguments used to justify the pantograph effect are
among these, the $Q^{\text{H}}_4$ optical mode discussed by Choi et al. (33) is of special interest as its symmetry is compatible with the pantograph effect discussed here. In summary, our original approach and results shed light on the issue of tuning magnetic ground states of matter with the use of external magnetic fields and pressure, by means of a clever combination of state-of-the-art experimental and computational tools.

Materials and Methods
Experimental. The high-quality single-crystal samples used in this work were prepared by the optical floating zone image furnace technique using self-flux as described elsewhere (34), oriented, and cut into $\sim 2 \times 2 \times 3$ mm$^3$ pieces for the magnetostriction experiment. Magnetostriction measurements were carried out using an optical fiber, furnished with a FBG, attached to the sample to detect length variations as a rapidly varying external magnetic field is applied (17). The reflection of light by the FBG at the Bragg wavelength shifts when the grating spacing changes. In our experimental setup, two different configurations were used to measure in-plane and out-of-plane magnetostriction. In the latter case, $\Delta c/c$ is measured with the fiber and magnetic field both along the crystallographic $c$ axis whereas in the former case, the fiber is bent around a circle of 0.6-inch diameter and kept in place with a stainless steel fine diameter tube to reach the sample at 90° from the $c$ axis (and magnetic field $H$) and thus obtain $\Delta a/a$.

Computational. Total energy calculations were performed with the Quantum Espresso (23) code. This code is based on DFT and uses the pseudopotential plane-wave method. The calculations were performed using ultrasoft pseudopotentials (35). For exchange and correlation, we used the GGA-PBE (36) augmented by a Hubbard $U$ term to improve the treatment of strongly correlated Cu-d$_{x^2-y^2}$ electrons. A value of the effective Hubbard $U = 10.3$ eV was determined in a 44-atom tetragonal cell, using the experimental structure determined at 300 K (3) with a ferromagnetic order and following the approach proposed in ref. 37. For structural relaxations, a plane-wave cutoff of 60 Ry and a $6 \times 6 \times 6$ Monkhorst-Pack (38) grid for the first Brillouin zone sampling were used. At the end of the relaxation procedure the total pressures were lower than 0.35 kbar and the forces were less than 10$^{-5}$ Rybohr.

Moreover, our calculations predict a strong effect ($\sim 10\%$ reduction) in the intradimer exchange integral $J$ as $a$ decreases, with no detectable variation in the interdimer counterpart $J'$. These results have implications in the reading of phase diagrams such as $H/J$ discussed by Matsuda et al. (29). As the $J/J'$ ratio increases with the applied magnetic field, the high-field part of the phase diagram should be read following a diagonal line oriented to the right. Indeed, the absence of the 2/5 plateau reported in the magnetization vs. field experiments in ref. 29 or the small stability region observed in the magnetostriction experiments in ref. 17 can be explained as being due to an increase of the exchange interaction ratio $J/J'$ in the high-field region.

Our results could also shed light on 2D models used so far to predict magnetization plateaus, as the expected changes in CuOCu angle and $J$ can have different effects on different models and help to sort them out according to prediction power. As we show, the reduction in $J$ comes alongside a drop in the volume of the crystallographic unit cell of SCBO that is usually the effect of applied pressures. In simpler words, our results also suggest that pressures of the order of a few gigapascals might be used to control the $J'/J$ parameter through the pantograph effect and therefore to drive SCBO out of the spin dimer ground state into plaquette or Néel order. Magnetic susceptibility vs. pressure and very recent neutron diffraction under pressure results (30, 31) support these ideas. We also note that low temperature active Raman modes have been identified as being correlated with the spin gap in SrCu$_2$(BO$_3$)$_2$.


