Quasi-two-dimensional Bose-Einstein condensation of spin triplets in dimerized quantum magnet Ba$_2$CuSi$_2$O$_6$Cl$_2$

Makiko Okada,$^1$ Hidekazu Tanaka,$^1$ Nobuyuki Kurita,$^1$ Kohei Johmoto,$^2$
Hidehiro Uekusa,$^2$ Atsushi Miyake,$^3$ Masashi Tokunaga,$^3$ Satoshi Nishimoto,$^{4,5}$
Masaaki Nakamura,$^6$ Marcelo Jaime,$^7$ Guillaume Radtke,$^8$ and Andrés Saúl$^9$

$^1$Department of Physics, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan
$^2$Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan
$^3$Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
$^4$Institute for Theoretical Solid State Physics, IFW Dresden, 01171 Dresden, Germany
$^5$Department of Physics, Technical University Dresden, 01069 Dresden, Germany
$^6$Department of Physics, Ehime University, Bunkyo-cho 2-5, Matsuyama, Ehime 790-8577, Japan
$^7$National High Magnetic Field Laboratory, and Materials, Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA
$^8$Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne Universités, Université Pierre et Marie Curie - Paris 6, UMR CNRS 7590, Museum National d’Histoire Naturelle, IRD UMR 206, 75005 Paris, France
$^9$Aix-Marseille University, Centre Interdisciplinaire de Nanoscience de Marseille-CNRS UMR 7325 Campus de Luminy, 13288 Marseille cedex 9, France

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We synthesized single crystals of composition Ba$_2$CuSi$_2$O$_6$Cl$_2$ and investigated its quantum magnetic properties. The crystal structure is closely related to that of the quasi-two-dimensional (2D) dimerized magnet BaCuSi$_2$O$_6$ also known as Han purple. Ba$_2$CuSi$_2$O$_6$Cl$_2$ has a singlet ground state with an excitation gap of $\Delta/k_B = 20.8$ K. The magnetization curve for two different field directions almost perfectly coincide when normalized by the $g$-factor except for a small jump anomaly for a magnetic field perpendicular to the $c$ axis. The magnetization curve with a nonlinear slope above the critical field is in excellent agreement with exact-diagonalization calculations based on a 2D coupled spin-dimer model. Individual exchange constants are also evaluated using density functional theory (DFT). The DFT results demonstrate a 2D exchange network and weak frustration between interdimer exchange interactions, supported by weak spin-lattice coupling implied from our magnetostriiction data. The magnetic-field-induced spin ordering in Ba$_2$CuSi$_2$O$_6$Cl$_2$ is described as the quasi-2D Bose-Einstein condensation of triplets.

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I. INTRODUCTION

Bose-Einstein condensation (BEC) is a fascinating macroscopic quantum phenomenon characteristic of system of bosons.\cite{2,1} BEC occurs not only in true bosonic particles\cite{3,2} but also in bosonic quasiparticles.\cite{3,2} Dimerized quantum magnets (DQMs) provide a stage to embody the quantum physics of interacting lattice bosons.\cite{3,2} In a DQM, two spins are dimerized by a strong antiferromagnetic (AFM) exchange interaction and these dimers are coupled via weak exchange interactions. DQMs usually have a gapped singlet ground state and exhibit magnetic-field-induced\cite{10,15} and pressure-induced\cite{16,21} quantum phase transitions (QPTs) to an ordered state. These QPTs can be described as the BEC of the $S_z = \pm 1$ components of the spin triplets called triplons.\cite{22,23} In pressure-induced BEC, the triply degenerate triplons are coupled via quantum critical point (QCP) into one amplitude mode,\cite{22} which can be interpreted as the Higgs mode, and two phase modes, which correspond to the Nambu-Goldstone modes.\cite{27} In magnetic-field-induced BEC of triplons with $S_z = +1$, the particle quantities of chemical potential $\mu$, triplon density $n$, and compressibility $\kappa = \partial n/\partial \mu$ correspond to the magnetic quantities of the external field $H$, total magnetization $M$ and magnetic susceptibility $\chi = \partial M/\partial H$, respectively, which are easily measured. A feature of triplon BEC is that the total number of triplons is controllable by tuning the magnetic field or pressure, in contrast to the BEC of true particles.

The magnetic-field-induced BEC of triplons in 3D DQMs has been studied experimentally for many systems.\cite{14,12} and the results observed were quantitatively or semiquantitatively described by the triplon BEC theory.\cite{15,22,23} On the other hand, in 2D systems, long-range ordering is suppressed by large quantum and thermal fluctuations, and topological ordering such as the Berezinskii-Kosterlitz-Thouless (BKT) transition\cite{28,30} and unusual quantum critical behavior are expected to occur. Recently, the BKT transition has been reported for the 2D DQM $C_{3h}$H$_{48}$Cu$_2$Fe$_6$O$_{12}$S$_2$.\cite{31} However, the understanding of 2D systems of interacting triplons is insufficient. For a detailed study of the
systems, a new 2D-like DQM, for which sizable single crystals are obtainable, is necessary. In this paper, we show that Ba$_2$CuSi$_2$O$_6$Cl$_2$, synthesized in this work, is close to an ideal 2D dimerized isotropic quantum magnet, which exhibits field-induced magnetic order in laboratory-accessible critical fields.

II. EXPERIMENTAL DETAILS

To synthesize single crystals of Ba$_2$CuSi$_2$O$_6$Cl$_2$, we first prepared Ba$_2$CuTeO$_6$ powder by a solid-state reaction. A mixture of Ba$_2$CuTeO$_6$ and BaCl$_2$ in a molar ratio of 1:10 was vacuum-sealed in a quartz tube. The temperature at the center of the horizontal tube furnace was lowered from 1100 to 800°C over 10 days. Plate-shaped blue single crystals with a maximum size of 3×3×1 mm$^3$ were obtained. These crystals were found to be Ba$_2$CuSi$_2$O$_6$Cl$_2$ from X-ray diffraction, where the silicon was provided by the quartz tube. The wide plane of the crystals was confirmed to be the crystallographic $ab$ plane by X-ray diffraction. We found that the quartz tube frequently exploded during cooling to room temperature after the crystallization process from 1100 to 800°C. To avoid hazardous conditions and damage to the furnace, a cylindrical nichrome protector was inserted in the furnace core tube.

The magnetic susceptibility of Ba$_2$CuSi$_2$O$_6$Cl$_2$ single crystal was measured in the temperature range of 1.8–300 K using a SQUID magnetometer (Quantum Design MPMS XL). The specific heat of Ba$_2$CuSi$_2$O$_6$Cl$_2$ was measured in the temperature range of 0–300 K using a physical property measurement system (Quantum Design PPMS) by the relaxation method. High-field magnetization measurement in a magnetic field of up to 45 T was performed at 4.2 and 1.4 K using an induction method with a multilayer pulse magnet at the Institute for Solid State Physics, University of Tokyo.

Magnetostriction of Ba$_2$CuSi$_2$O$_6$Cl$_2$ was measured at National High Magnetic Field Laboratory, Los Alamos National Laboratory. Variations in the sample length $L$ as a function of the temperature and/or magnetic field, $\varepsilon(H) = \Delta L/L(H) = [L(H, T) - L(H_0, T_0)]/L(H_0, T_0)$, were measured using a fiber Bragg grating (FBG) technique consisting of recording spectral information of the light reflected by a 0.5-mm-long Bragg grating inscribed in the core of a 125 µm telecom optical fiber. The FBG section of the fiber is attached to the sample to be studied, and changes in the grating spacing are driven by changes in the sample dimensions when the temperature or magnetic field is changed. This technique has a demonstrated resolution of $\Delta L/L \approx 10^{-7}$ that is virtually immune to the electromagnetic noise characteristic of pulsed magnetic fields but is somewhat sensitive to mechanical vibrations. Capacitor-bank-driven pulsed magnets were used to produce 25 ms magnetic field pulses up to 60 T.

| Atom  | $x$  | $y$  | $z$  | $U_{eq}$ |
|-------|------|------|------|---------|
| Ba(1) | 2715(1) | 6230(1) | 1093(1) | 25(1) |
| Ba(2) | 0     | 3917(1) | 1045(1) | 24(1) |
| Ba(3) | 5000  | 3535(1) | 1045(1) | 27(1) |
| Cl(1) | 2012(5) | 3562(3) | 429(3)  | 51(2) |
| Cl(2) | 0     | 1390(9) | 569(4)  | 60(3) |
| Cl(3) | 5000  | 1244(6) | 585(5)  | 73(3) |
| Cu(1) | 2503(1) | 3783(2) | 1761(1) | 17(1) |
| O(1)  | 1747(8) | 4919(9) | 1819(7) | 24(3) |
| O(2)  | 3693(9) | 4495(8) | 1820(7) | 26(3) |
| O(3)  | 1231(8) | 6241(8) | 2728(6) | 21(2) |
| O(4)  | 0     | 4941(12)| 2251(9) | 22(4) |
| O(5)  | 3278(8) | 2565(8) | 1827(6) | 20(2) |
| O(6)  | 0     | 2532(11)| 2750(8) | 19(3) |
| O(7)  | 1334(8)| 2960(8) | 1822(6) | 20(2) |
| Si(1) | 1111(4)| 5122(3)| 2493(5) | 21(1) |
| Si(2) | 1109(4)| 2376(3)| 2499(2) | 15(1) |

III. COMPUTATIONAL DETAILS

Band structure and total energy calculations were performed with the QUANTUM ESPRESSO [58] suite of codes based on density functional theory (DFT) and using the pseudopotential plane-wave method. The calculations were performed using ultrasoft pseudopotentials [35] with plane-wave and charge density cutoffs of 60 Ry and 400 Ry, respectively, and a 4 × 4 × 2 Monkhorst-Pack [59] grid for the first Brillouin zone sampling of the 104-atom base-centered orthorhombic unit cell of Ba$_2$CuSi$_2$O$_6$Cl$_2$. Exchange and correlation were taken into account using the generalized gradient approximation of Perdew, Burke and Ernzerhof [37] (GGA-PBE) augmented by a Hubbard $U$ term to improve the treatment of strongly correlated Cu-3d electrons. A value of $U_{scf} = 10.4$ eV for the effective self-consistent Hubbard term was determined for the 104-atom unit cell following the approach described in Refs. [38] and [39], using the experimental structure determined at 300 K and a ferromagnetic order.
Maximally localized Wannier function (MLWF) interpolation of the band structure was performed using WANNIER90, which allows the extraction of effective hopping integrals between magnetic orbitals. The calculation of magnetic couplings was carried out within the broken symmetry formalism, i.e., by mapping total energies corresponding to various collinear spin arrangements within a supercell onto the Heisenberg Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \sum_{\langle i,j \rangle} J_{ij} S_i \cdot S_j,$$

where $\mathcal{H}_0$ is the spin-independent part of the Hamiltonian, $J_{ij}$ are the magnetic couplings to be determined, and $S_i$ and $S_j$ are, in our case, the $S_z = 1/2$ 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 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 in the form of the Ising Hamiltonian

$$\epsilon^\text{DFT}_\alpha = \langle \alpha | \mathcal{H} | \alpha \rangle = \epsilon_0 + \frac{1}{4} \sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j$$

with $\sigma_i = \pm 1$. In strongly localized systems, such as 3$d$ transition-metal oxides, Eq. 2 can be employed to model large sets of spin configurations, and a least-squares minimization of the difference between the DFT and Ising relative energies can be applied to obtain a numerical evaluation of the couplings.

IV. CRYSTAL STRUCTURE

We performed a structural analysis at room temperature using a RIGAKU R-AXIS RAPID three-circle X-ray diffractometer equipped with an imaging plate area detector. Monochromatic Mo-K$_\alpha$ radiation with a wavelength of $\lambda = 0.71075$ Å was used as the X-ray source. Data integration and global-cell refinements were performed using data in the range of $3.119^\circ < \theta < 27.485^\circ$, and absorption correction based on face indexing and integration on a Gaussian grid was also performed. The total number of reflections observed was 17599, among which 2252 reflections were found to be independent and 1521 reflections were determined to satisfy the criterion $I > 2\sigma(I)$. Structural parameters were refined by the full-matrix least-squares method using SHELXL–97 software. The final $R$ indices obtained for $I > 2\sigma(I)$ were $R = 0.0773$ and $wR = 0.1638$. The crystal data are listed in Table I. The chemical formula was confirmed to be Ba$_2$CuSi$_2$O$_6$Cl$_2$ (BCuSOC). The structure of BCuSOC is orthorhombic $Cmca$ with cell dimensions of $a = 13.8917(12)$ Å, $b = 13.8563(11)$ Å, $c = 19.6035(15)$ Å and $Z = 16$. Its atomic coordinates and equivalent isotropic displacement parameters are shown in Table II.

The structure of BCuSOC, closely related to that of Ba$_2$CoSi$_2$O$_6$Cl$_2$ (CoSOC), is orthorhombic $Cmca$ with cell dimensions of $a = 13.8917(12)$ Å, $b = 13.8563(11)$ Å and $c = 19.6035(15)$ Å. The crystal structure viewed along the $b$, $a$ and $c$ axes is illustrated in Figs. (a), (b) and (c), respectively. The crystal structure comprises CuO$_4$Cl pyramids with a Cl$^-$ ion at the apex. Magnetic Cu$^{2+}$ with spin-1/2 is located approximately at the center of the base composed of O$^{2-}$, which is parallel to the $ab$ plane. Two neighboring CuO$_4$Cl pyramids along the $c$ axis are placed with their bases facing each other. The CuO$_4$Cl pyramids are linked via SiO$_4$ tetrahedra in the $ab$ plane, as shown in Fig. (c). The atomic linkage in the $ab$ plane is approximately the same as that of BaCuSi$_2$O$_6$. Two bases of neighboring CuO$_4$Cl pyramids are rotated in opposite directions around the $c$ axis, as observed in BaCuSi$_2$O$_6$. Such rotation of the bases of the CoO$_4$Cl pyramids is absent in Ba$_2$CoSi$_2$O$_6$Cl$_2$. 

FIG. 1: (Color online) Crystal structure of Ba$_2$CuSi$_2$O$_6$Cl$_2$ viewed along the (a) $b$ axis, (b) $a$ axis and (c) $c$ axis.
V. RESULTS AND ANALYSES

Figure 2(a) shows the temperature dependence of the magnetic susceptibilities $\chi(T)$ for BCuSOC with $H\parallel c$ and $H\perp c$. The susceptibility data are normalized by the $g$-factors of $g_\parallel = 2.32$ and $g_\perp = 2.06$, determined from electron paramagnetic resonance data at room temperature. The normalized susceptibilities $(2/g)^2\chi(T)$ almost perfectly coincide above 6 K, which indicates that the anisotropy of the magnetic interactions is very small. The susceptibility has a rounded maximum at $T_{\text{max}} \approx 18$ K, followed by a rapid decrease with decreasing temperature. No anomaly indicative of a phase transition was observed below 4 K, which is characteristic of Heisenberg spin dimer magnets with a gapped singlet ground state.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2}
\caption{(Color online) (a) Temperature dependence of magnetic susceptibilities of BCuSOC measured for $H\parallel c$ and $H\perp c$. The susceptibilities are normalized by the $g$-factors of $g_\parallel = 2.32$ and $g_\perp = 2.06$. The solid line denotes the fit obtained using Eq. (3). (b) Temperature dependence of total specific heat divided by the temperature measured at zero magnetic field.}
\end{figure}

It is natural to assume that the two Cu$^{2+}$ spins located on the bases of neighboring CuO$_4$Cl pyramids along the $c$ axis are coupled to form an AFM dimer. Because magnetic excitation in BaCuSi$_2$O$_6$ is dispersive in the $ab$ plane and dispersionless along the $c$ direction [10], BCuSOC can approximate a 2D coupled spin dimer system with the exchange network shown in Fig. 3. This is confirmed by the DFT calculation shown later. Because the crystal structure is nearly tetragonal, we can assume that $J_{11}^a = J_{22}^a = J_{11}^b = J_{22}^b \equiv J_p$ and $J_{12}^a = J_{12}^b = J_{21}^a = J_{21}^b \equiv J_d$.

When interdimer exchange interactions are treated as mean fields, the magnetic susceptibility is expressed by

$$\chi(T) = \frac{g^2 T B^2 \beta N}{\exp(\beta J) + 3 + \beta J},$$

where $\beta = 1/(k_B T)$, $N$ is the number of spins, $J$ is the intradimer exchange interaction and $J'$ is the sum of the interdimer interactions acting on one spin in a dimer, which is given for the present system by $J' = 4(J_p + J_d)$. Fitting Eq. (3) with the Curie and constant terms to the experimental susceptibility for $H\parallel c$, we evaluate $J$ and $J'$ as $J/k_B = 29.4$ K and $J'/k_B = 13.8$ K, which are consistent with $J/k_B = 28.1$ K and $J'/k_B = 17.2$ K evaluated from the analysis of the magnetization curve, shown below. The solid line in Fig. 2(a) denotes the fit, which excellently reproduces the experimental susceptibility.

Figure 2(b) shows the total specific heat divided by the temperature of BCuSOC measured at zero magnetic field. No anomaly indicative of a structural phase transition was observed down to 0.5 K, although in BaCuSi$_2$O$_6$, a structural phase transition was observed at $T_s \approx 100$ K [50]. In BaCuSi$_2$O$_6$, there are three types of dimer with different exchange interactions $J$ below $T_s$ [51]. The absence of the structural phase transition in BCuSOC indicates that all the dimers are likely magnetically equivalent down to 0.5 K. A Schottky-like anomaly is observed around 10 K owing to the excitation gap of $\Delta/k_B = 20.8$ K, which is determined through the high-magnetic-field magnetization measurement described below.

Figure 4(a) shows the magnetization curves of BCuSOC and their field derivatives measured at 1.4 K for $H\parallel c$ and $H\perp c$. The magnetization data are normalized by the susceptibility data.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3}
\caption{(Color online) 2D model of the exchange network in Ba$_2$CuSi$_2$O$_6$Cl$_2$. Thick solid lines represent the intradimer exchange interactions $J_p$ and $J_d$ ($\alpha, \beta = 1, 2$).}
\end{figure}
FIG. 4: (Color online) (a) Magnetic-field dependence of magnetization $M$ and its field derivative $dM/dH$ for BCuSOC measured at 1.4 K for $H \parallel c$ and $H \perp c$, which are normalized by the $g$-factors. An arrow indicates an anomaly in $dM/dH$ for $H \perp c$ owing to a phase transition accompanied with a small magnetization jump. (b) Axial magnetostriction $\varepsilon_a(H)$, with $H \perp c$ and $H \parallel c$, at $T = 1.3$ K after subtraction of the smooth background of similar magnitude measured at $T = 10$ K. The axial magnetostriction along and perpendicular to the $c$ axis (at $(g/2)H = 25$ T) show magnitudes and signs which, in a magnetically isotropic system, would indicate conservation of the unit cell volume. (c) Comparison between experimental and theoretical magnetization curves for $H \parallel c$. The theoretical result was obtained using exact diagonalization (ED) for a 32-site spin cluster.
the GGA-PBE paramagnetic bands of the dominant Cu-3d_{x,y} character was carried out. The results are shown in Figure 5. The corresponding hopping integrals are summarized in Table III An estimate of the AFM contribution to the magnetic couplings can indeed be achieved through mapping of the paramagnetic band structure onto a single-band Hubbard model at half filling, eventually reducing to an AFM Heisenberg model in the strongly correlated limit. In this approach, the effective interaction is given by \( J_{\alpha\beta}^{AFM} = 4t_{\alpha\beta}^2/U_{\text{eff}} \). It can be readily seen from Table III that the largest hopping integral \( t \) occurs between two Cu\(^{2+}\) ions located within the same structural dimer, revealing the potential presence of a leading nearest-neighbor AFM coupling. The next largest interactions \( (t_{12}^a = t_{21}^a = t_{12}^b = t_{21}^b = t_d) \) couple two Cu\(^{2+}\) ions belonging to one of the four neighboring dimers but located in adjacent planes of the same bilayer. The remaining interactions within the bilayer \( (t_{11}^a = t_{22}^a = t_{11}^b = t_{22}^b = t_p) \) are an order of magnitude smaller, and inter-bilayer interactions \( (t_\perp) \) are vanishingly weak. This hierarchy in the order of magnitude can easily be seen in Figure 6 using a simple 2D tight-binding analysis. The use of a 2D model is justified by the absence of a sizable dispersion along \( \Gamma \rightarrow Z \) or \( S \rightarrow R \), and therefore, the absence of sizable inter-bilayer interactions. Neglecting the inter-bilayer interactions \( t_\perp \) and \( t'_{\perp} \), the Cu-3d_{x,y} band energy dispersions are given by

\[
\begin{align*}
\epsilon_{a,\pm}(k) &= \epsilon_d + t \pm 4(t_p + t_d) \cos(\pi k_x) \cos(\pi k_y), \\
\epsilon_{b,\pm}(k) &= \epsilon_d - t \pm 4(t_p - t_d) \cos(\pi k_x) \cos(\pi k_y),
\end{align*}
\]

where \( t_p \) is the interdimer hopping parallel to the \( ab \) plane, \( t_d \) is the diagonal interdimer hopping and \( k = (k_x, k_y) \) is the 2D reciprocal vector in units of the reciprocal lattice basis vectors. These two groups of bands are shifted with respect to each other by twice the intradimer hopping \( t \), whose value can readily be determined at \( S \), or to a lesser extent because of additional splittings occurring under the effect of further couplings at \( T \) or \( Y \). The band dispersion, as observed along \( \Gamma \rightarrow S \) for instance, is directly related to the interdimer interaction \( t_d \) either through \( (t_p + t_d) \) for the lower-energy group of bands or through \( (t_p - t_d) \) for the higher-energy group.

These results provide a clear picture of the dominant AFM magnetic couplings in Ba\(_2\)Cu\(_2\)Si\(_2\)O\(_6\)Cl\(_2\): the largest interaction \( J_{\alpha\beta}^{AFM} \) arises within the structural dimers, which are then coupled together by a weaker interdimer interaction \( J_{d}^{AFM} \). Their ratio can be estimated to be \( J_{d}^{AFM}/J_{\alpha\beta}^{AFM} = (t_d/t) \approx 0.22 \). Other interactions, arising either within the bilayers or between them, exhibit a negligible AFM component.

Figure 7 shows the MLWF corresponding to the band interpolation presented in Fig. 5. Its dominant Cu-3d_{x,y} character is clearly apparent, as well as the large antibonding tails held by the four coordinating oxygen atoms O1, O2, O5 and O7. Note however, that non-negligible components are also visible on

VI. DENSITY FUNCTIONAL CALCULATIONS

To assess the validity of our discussion on the basis of a microscopic analysis, isotropic magnetic couplings were estimated using DFT calculations 34, 35. As the first step, Wannier function interpolation 41 of the ED calculation, we cannot determine whether the parallel \( J_p \) or diagonal \( J_d \) interdimer interaction is dominant. This point will be addressed below using DFT calculations.

For \( H \perp c \), \( M(H) \) shows a small jump at \( M \approx 0.5M_s \), which is evident in \( dM/dH \) (Fig. 4a). The magnetization anomaly observed upon sweeping the magnetic field upward and downward is intrinsic. It is considered that the magnetization jump arises from spin reorientation. Because the inversion symmetry with respect to the midpoint of the two spins in a dimer is absent, the Dzyaloshinskii-Moriya (DM) interaction of the form \( D_i \cdot (S_{\parallel} \times S_{\parallel}) \) between spins \( S_{\parallel} \) can be finite, although it is small. The \( D \) vector must be in the \( ac \) plane because of the twofold axis passing through the midpoint of the dimer along the \( b \) axis 53. The magnetization curve for \( H \parallel c \) shows no anomaly, hence the \( a \) axis component of the \( D \) vector will be small. The \( c \) axis components of the \( D \) vectors on the neighboring dimers should be antiparallel dueowing to the mirror plane at \( a/2 \) and the glide planes at \( \pm c/4 \). The DM interaction is usually accompanied with anistropy of the form \( (S_{\parallel} \cdot D_{\parallel})(S_{\parallel} \cdot D_{\parallel}) \) (known as the KSEA interaction) 52, 53. The KSEA interaction favors spins parallel to the \( D \) vector, which is assumed to be parallel to the \( c \) axis, while the DM interaction favors spins perpendicular to the \( c \) axis. Thus, competition between the DM and KSEA interactions occurs, likely giving rise to a spin reorientation transition for \( H \perp c \).
TABLE III: Magnetic couplings in Ba$_2$CuSi$_2$O$_6$Cl$_2$: Cu-Cu distances $d$ [Å], hopping integrals $t$ [meV] and magnetic couplings $J$ calculated using GGA+$U_{\text{act}}$ [K]. Hopping integrals are related to the AFM component of the couplings through the relation $J_{\alpha\beta}^{\text{FM}} = 4t_{\alpha\beta}^2/U_{\text{eff}}$ where $U_{\text{eff}}$ is the effective Hubbard repulsion term. Positive couplings imply AFM interactions.

| $d$ (in Å) | $t_{11}$ | $t_{12}$ | $t_{11}$ | $t_{12}$ | $t_{12}$ | $t_{12}$ | $t_{12}$ | $t_{12}$ | $t_{12}$ | $t_{12}$ |
|-----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 2.90      | 6.95    | 6.94    | 6.93    | 6.93    | 7.53    | 7.53    | 7.51    | 7.51    | 7.68    | 7.77    |
| $t$ (in meV) | -64 | 5 | 8 | 5 | 5 | 28 | 28 | 32 | 32 | 0 | 0 |

| $J$ (in K) | $J_\parallel$ | $J_\perp$ | $J_\parallel$ | $J_\perp$ |
|-----------|--------------|----------|--------------|----------|
| 30.5      | -0.2         | 5.9      | -0.3         |          |

FIG. 6: (color online) MLWF centered on a Cu site. Large antibonding O-2$p$ tails are clearly visible on the Cu coordinating oxygen atoms.

FIG. 7: (color online) Graphical representation of the results obtained by the least-squares fitting procedure employed to evaluate the magnetic couplings: optimized energies calculated with the Ising Hamiltonian are represented as a function of the DFT + $U_{\text{act}}$ relative energies. Positive couplings correspond to AFM interactions according to Eq. (4).
VII. CONCLUSION

In conclusion, we have presented the first structural analysis, magnetization and magnetoelastic measurements on Ba$_2$CuSi$_2$O$_6$Cl$_2$. The magnetic susceptibilities and magnetization curves for different field directions coincide almost perfectly when normalized by the respective $g$-factors, which indicates that the magnetic anisotropy is very small. The observed magnetization data are excellently reproduced using exact-diagonalization computations based on the 2D coupled dimer model illustrated in Fig. 4(d). The 2D exchange model was also confirmed by DFT. Thus, Ba$_2$CuSi$_2$O$_6$Cl$_2$ closely approximates the ideal 2D dimerized Heisenberg quantum magnet. The quantum critical behavior near both critical fields $H_c$ is and the nature of the spin state above $H_c$ are of great interest and currently under investigation.

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