Two types of adjacent dimer layers in the low temperature phase of BaCuSi$_2$O$_6$

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The low-temperature crystal structure of BaCuSi$_2$O$_6$ has been investigated with high-resolution synchrotron x-ray and neutron powder diffraction techniques and has been found to be on average (ignoring the incommensurate modulation) orthorhombic, with the most probable space group $Ibam$. The Cu–Cu dimers in this material are forming two types of layers with distinctly different interatomic distances. Subtle changes also modify the partially frustrated interlayer Cu–Cu exchange paths. The present results corroborate the interpretation of low-temperature nuclear magnetic resonance and inelastic neutron scattering data in terms of distinct dimer layers.

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I. INTRODUCTION

Intense studies of field–induced quantum phase transitions (QPTs) in various magnetic insulators continue to enrich our knowledge of the possible quantum ground states of matter. Structurally dimerized quantum spin systems play a leading role in these studies; the classes of field–induced QPTs known to date in these systems are well summarized in Refs.\textsuperscript{3,4} For magnetic interactions with weak or no frustration, the kinetic energy of the triplet quasiparticles in such systems is dominant and the triplet states with $S=1$ are gapped;\textsuperscript{1,2} Cu interactions within the Cu dimers in adjacent layers ($\sim 5\,\text{Å}$) are much larger. Thus, to a great extent, the ground state of the system is determined by the Cu–Cu interactions within the dimers.\textsuperscript{1,2,3,5}

At zero magnetic field, the ($S=1/2$) Cu$^{2+}$ ions are paired antiferromagnetically, while the degenerate excited triplet states with $S=1$ are gapped\textsuperscript{6} thus the compound possesses an essentially singlet ground state with $S=0$ at $H=0$. Upon application of a mag-
netic field, the excited triplet states are Zeeman split with the energy scale of the splitting being proportional to magnetic field. At a critical magnetic field value of $H_c \sim 23.5$ T, the energy of the lowest triplet state with $S_z = +1$ becomes lower than that of a singlet state with $S = 0$, and a magnetic field-induced BEC of the excitations occurs. The population of the bosons (measured as the magnetization of the sample) may be precisely tuned by the magnetic field. Another intriguing phenomenon observed in BaCuSi$_2$O$_6$ next to this QPT is a dimensional crossover around 1 K from a 3D into a 2D regime with lowering temperature. To explain this feature, perfect frustration between adjacent Cu$_2$(SiO$_3$)$_4$ layers was assumed. Alternatively, the hypothesis has emerged that a structural modulation along the $c$ axis combined with nonperfect frustration is the sole reason for the lowered dimensionality. As a unifying theory, a possibility has been proposed that the combined effect of the structural modulation along the $c$ axis and the nearly perfect interlayer frustration is a reason for the observed dimensional crossover.

In attempts to build a theory of this QPT, the compound was originally assumed to possess the same square motif of the Cu – Cu dimers at low temperatures as at room temperature, resulting in three relevant coupling constants entering the spin Hamiltonian: the intradimer, interdimer, and interlayer couplings.

However, high resolution inelastic neutron scattering (INS) data were clearly at odds with this picture. Furthermore, a first-order structural phase transition at $\sim 100$ K has been discovered by Stern et al. and reported by Samulon et al., which necessarily states that the true spin Hamiltonian of the system is more complex than originally thought. The method of single crystal diffraction used in Ref. confirmed the transition into an orthorhombic (or weakly monoclinic) structure. Moreover, it allowed for observation of satellite peaks indicating an incommensurate modulation in the low-temperature (LT) phase of BaCuSi$_2$O$_6$. Here we use in contrast a combination of high-resolution x-ray and neutron powder diffraction techniques in order to determine the average crystal structure of the LT phase of BaCuSi$_2$O$_6$.

II. EXPERIMENTAL

A. Synthesis

Polycrystalline samples of BaCuSi$_2$O$_6$ were prepared by solid-state reaction. Powders of BaCO$_3$, CuO, and SiO$_2$ were weighted to the prescribed ratios, mixed, and well ground. The mixture was calcined at 900°C in air for 20 h. The resulting powders were pulverized, isostatically pressed into a rod shape ($\sim 5$ mm diameter, $\sim 50$ mm length) and sintered again at 1010°C in air for 20 h.

B. Powder diffraction experiments

The powder diffraction experiments have been carried out with two high-resolution diffractometers: the Powder Diffraction station of the Materials Sciences Beamline (MS-PD) at the Swiss Light Source and the high-resolution powder neutron diffractometer HRPT at the spallation neutron source SINQ, both at Paul Scherrer Institute in Villigen.

At the MS-PD station, the synchrotron x-ray diffraction data were collected on a powder sample enclosed in a capillary of a 0.3 mm diameter, which was placed in a Janis flow-type cryostat. The Microstrip Mythen-II detector was used, which allowed for high counting rates while maintaining the high resolution which was essentially sample-conditioned. The typical counts of $\sim 2 \times 10^5$ in the strongest peaks were achieved within $\sim 1$ minute. On cooling, the diffraction patterns were collected with 1 K steps in the temperature range from 154 to 64 K, and with 2 K steps in the temperature range from 64 to 12 K. After collecting the lowest temperature dataset at 4 K, the data were collected on heating the sample in the temperature range from 5 to 123 K with typically 1...2 K steps and from 128 to 178 K with 5 K steps, in order to observe the transition both on cooling and on heating and to characterize the hysteresis thereof.

At HRPT, a bigger amount ($\sim 1$ g) of the very same powder sample of BaCuSi$_2$O$_6$ was enclosed into a vanadium can of a 6 mm diameter, and the data were collected using a close-cycle refrigerator at 130 K (well above the transition on cooling) and at 13 K (far below the transition) in the instrument setup with the highest resolution. The ultimate resolution was needed because the orthorhombic splitting of the peaks of the parent tetragonal RT structure characterized by an orthorhombicity parameter defined as $2 | a_{\text{orth}} - b_{\text{orth}} | / (a_{\text{orth}} + b_{\text{orth}})$ amounts only to $\sim 1.7 \times 10^{-3}$.

The data of the neutron diffraction experiment were used for the structure determination, and for the precise refinement of the structural parameters at low temperature, while the synchrotron x-ray powder diffraction data have mainly been used for indexing, space group selection and refinement of the temperature dependence of the main structural parameters, as well as for identifying all the impurity phases present. The following impurities have been determined in the powder sample: BaCu$_2$Si$_2$O$_7$ (4.4 % wt.), BaCu$_4$Si$_4$O$_{18}$ (1.3 % wt.), Ba$_4$Si$_6$O$_{16}$ (1.1 % wt.), Ba$_2$SiO$_4$ (0.3 % wt.), and Cu$_2$O (0.1 % wt.). Approximately 93 % wt. of the powder sample is the main BaCuSi$_2$O$_6$ phase. While treating the neutron data with $\sim 5000$ counts in the strongest peak, the only relevant impurity which was definitely seen in the diffraction pattern and correspondingly input into the refinements was BaCu$_2$Si$_2$O$_7$ (4.4 % wt.); the others were undetectable, and thus were not considered.

The RT crystal structure model (Ref. [22]) has been unambiguously confirmed by the Rietveld refinements based on both synchrotron x-ray and neutron data above the
The LT structural phase transition in BaCuSi$_2$O$_6$ is clearly seen in both neutron and x-ray diffraction patterns, and is most evident in the temperature-dependent x-ray data. Illustrations of the transition are given in Figs. 2 and 3. While all the peaks get a little narrower on cooling below the transition, we do not observe any of them to broaden. Instead, some remain single peaks, and some are splitting. The peak (2,2,12) at $\sim 23.1^\circ$ transforms into a pair of (4,6,8)/(6,4,8) which are not resolved, since the amplitudes of their scattering vectors are too close to each other. The backward phase transition on heating manifests itself (see Fig. 3) as a recovery of the diffraction pattern to that of the RT crystal structure, yet it occurs at a higher temperature.

The LT synchrotron x-ray diffraction pattern of BaCuSi$_2$O$_6$ showing clear splitting of the diffraction peaks $(hkl)$ with $h \neq k$ of the parent room temperature tetragonal crystal structure (space group $I4_1/acd$) has been indexed on the orthorhombic unit cell with lattice constants (at $T = 4$ K) $\{a,b,c\} = \{9.951 \text{ Å}, 9.968 \text{ Å}, 22.239 \text{ Å}\}$. From the systematic absences it has been found that the most probable space group is body-centered, and all the relevant possibilities have been checked for the structure determination. In fact we have performed the structure determination for all space groups and combinations of $(a,b,c)$, which did account for all diffraction peaks observed, although for many of these some of the calculated peaks were actually absent in the experimental pattern. Having done so, we may exclude any chance for having missed the true solution. The structure determinations have been carried out on a neutron diffraction dataset taken at $T = 13$ K, either with the program FOX$^{27}$ or by direct symmetry reduction in cases where it was possible and straightforward. All the models have been checked with extensive Rietveld refinements (done with the program FULLPROF$^{28}$) of their parameters from both the synchrotron x-ray and neutron powder diffraction patterns.

While going from higher to lower symmetries in the orthorhombic syngony, already the space group $Ibca$ (No. 73), which is a direct subgroup of the RT structure space group $I4_1/acd$, gives the first sensible solution. Yet the next group $Ibam$ (No. 72) supplies a definitely better model. Compared to the $Ibca$ model, the model in $Ibam$ provides a significant improvement of the agreement factors: $\chi^2$ decreases from 4.33 to 2.66, and the Bragg R-factor – from 7.05 to 4.80. Both structure models are in fact slight distortions of the RT tetragonal structure with $I4_1/acd$ symmetry, but are having very essential difference between each other from the point of view of the geometry of the Cu – Cu dimer layers and their stacking along the direction perpendicular to the Cu$_2$(SiO$_3$)$_4$ layers. The unique Cu atom in the RT structure model is being split into two distinct atoms in both models, but in the case of the $Ibca$ model they are forming just one type of Cu–Cu dimer layer, while the correct $Ibam$ model contains two distinctly different Cu – Cu dimer layers, and these will be discussed below. The Rietveld refinement plot obtained with the neutron data is shown in Fig. 4.

The refined parameters of the LT crystal structure are given in Table II and the most relevant interatomic distances in Table III. The schematic representation of the crystal structure of the LT phase of BaCuSi$_2$O$_6$ is given.

### III. RESULTS

#### A. Low-temperature crystal structure of BaCuSi$_2$O$_6$

The LT structural phase transition in BaCuSi$_2$O$_6$ has been checked for the structure determination. In fact we have performed the structure determination for
in Fig. 5.

Unlike in the single crystal experiments reported in Ref. [24], our study carried out by powder diffraction could not reveal the presence of any incommensurate peaks due to their relative weakness: According to Ref. [24], the central Bragg peaks did have to be scaled down by a factor of \(10^3\) to display on the same scale with the satellite incommensurate modulation peaks. Such dynamic ranges are inaccessible for powder diffraction, and in this sense, the presence of the incommensurate modulation did not hinder the determination of what we believe to be a most probable model for the average LT crystal structure of BaCuSi\(_2\)O\(_6\).

An interesting feature is observed in the geometry of the Cu\(_2\)(SiO\(_4\))\(_4\) layers which is very relevant for the interpretation of low-temperature magnetic properties: Mutual rotation of the CuO\(_4\) coordination polyhedra in the Cu-dimer layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on the Cu1–Cu2 layers, characteristic for the RT structure on

![FIG. 5. (Color online) Schematic representation of the crystal structure of the LT phase of BaCuSi\(_2\)O\(_6\). In the right panel, only the Cu–Cu dimers are shown. The Cu1–Cu1 distance of 2.774(6) Å is much longer than the Cu2–Cu2 with 2.701(6) Å. For the inter-layer coupling paths, Cu1–Cu2 (shown in thin lines in the right figure), there are always two pairs of slightly inequivalent bond distances (see Table I).](image)

![FIG. 4. (Color online) Rietveld refinement of the crystal structure parameters of the low-temperature (LT) phase of BaCuSi\(_2\)O\(_6\) from the neutron powder diffraction data. The observed intensity, calculated profile, and difference curve are shown. The rows of ticks at the bottom correspond to the calculated diffraction peak positions of the phases (from top to bottom): BaCuSi\(_2\)O\(_6\) - orthorhombic LT structure, BaCu\(_2\)Si\(_2\)O\(_7\) impurity (∼ 4.4 % w.t.)](image)
BaCuSi$_2$O$_6$, is only preserved in the layers with shorter Cu–Cu dumbbell distances. This feature is illustrated in Fig. 6. At 130 K, in the tetragonal phase, all the Cu–Cu dimer layers are equivalent and the CuO$_4$ coordination polyhedra look like squares slightly turned (∼19°) with respect to each other in each Cu–Cu dumbbell around its axis [Fig. 6(a): view along the c direction of the unit cell]. At low temperature, only the Cu2–Cu2 dimer layer with shorter Cu–Cu distances, shown on the left of Fig. 6(b), preserves this feature (the mutual rotation angles of the Cu2O$_4$ squares with respect to each other are on the order of ∼21...22°), and the Si$_4$O$_{12}$ rings in these layers are also (same as at 130 K) nearly squares. In contrast to this, the Cu1–Cu1 dimer layer with longer Cu–Cu distances, shown on the right of Fig. 6(b), the CuO$_4$ coordination polyhedra are not turned with respect to each other. The Si$_4$O$_{12}$ 4-member rings in the Cu1–Cu1 dimer layers show clear deviations from the ideal square shape, forming a checkerboard type of ordering of their elongation directions along one of the a–b plane diagonals. The intralayer Cu–Cu distances are identical in both types of layers in our model, yet it is too hard to quantify the obvious differences in the exact intralayer exchange paths between the dimers, which are obviously nonequivalent for the layers with the shorter and the longer Cu–Cu dimers.

B. First-order character of the transition

In agreement with the results already reported in Ref. 24, the structural transition we observe in BaCuSi$_2$O$_6$ is of first order. The refined unit cell volumes, as well as the weight proportions of the tetragonal and orthorhombic phases on cooling and on heating, are shown in Fig. 7. The observed discontinuity in the unit cell volume at the transition is ∼1%. The 50 : 50 proportions of the phases are reached at ∼89.7 K on cooling and at ∼107.2 K on heating. The width of the hysteresis is thus ∼17.5 K.
C. Possible alternative structure models

Dealing with the neutron powder dataset with limited intensity does not in principle exclude the possibility of having missed the lowering of the symmetry just due to the fact that the very weak diffraction intensities may potentially be confused with systematic absences. Having carried out an exhaustive search in the orthorhombic syngony for alternative crystal structure models of the LT phase of BaCuSi$_2$O$_6$, and upon carrying out careful refinements of their parameters, we can as well list all other possible structure models providing comparable agreement factors. It turns out that all alternative possibilities which deserve being considered are limited to the subgroups of the space group $Ibam$.

In Table III we have summarized all hypothetically possible models for the structure of the LT phase of BaCuSi$_2$O$_6$ providing plausible refinements, along with the key values — the numbers of the independent unique Cu—Cu dimer layers, the lengths of Cu—Cu dimers, some statistical indicators for the complexities of the models, and the corresponding agreement factors of the refinements. We find it inappropriate to present here all the structure models in details. The group-subgroup transformations are straightforward, and any models will be supplied on request. The general trend is that all alternative possibilities provide a pattern of the Cu — Cu dimer layers either very similar to or even more complex than that in our model with the space group $Ibam$ (Tables I and II). For some of them we have not 2 but 4 independent Cu — Cu dimer layers. Since the apparent improvement in agreement factors of the refinements for lower symmetries is only achieved when the number of independent atoms and refinable parameters is getting very high, and due to the obvious similarity to the highest symmetry model with the space group $Ibam$ (Tables I and II), we strongly tend to believe that the true structure of the LT phase of BaCuSi$_2$O$_6$ may sufficiently well and adequately be described by our model with the space group $Ibam$. Some later studies with higher precision may one day show slight deviations from this model to one of those listed in Table III.

| SG Set | $N_a, N_b$ | $N_{Cu}, N_D$ | Cu — Cu, Å | $\chi^2, R_p$ |
|--------|------------|---------------|-------------|----------------|
| 72 $Ibam$ | 14, 30 | 2, 2 | 2.701(6)/2.774(6) | 2.66, 4.80 |
| 60 $Pbcm$ | 21, 59 | 2, 2 | 2.713(6)/2.768(6) | 2.32, 4.41 |
| 57 $Pbcm$ | 25, 63 | 2, 2 | 2.705(6)/2.770(6) | 2.55, 4.69 |
| 56 $Pccm$ | 22, 58 | 4, 2 | 2.71(2)/2.78(3) | 2.42, 4.53 |
| 55 $Pbam$ | 26, 62 | 4, 4 | 2.71(2)/2.70(2)/2.86(2)/2.70(2) | 2.59, 4.75 |
| 50 $Pbam$ | 24, 56 | 4, 4 | 2.71(2)/2.77(3)/2.70(2)/2.77(3) | 2.36, 4.45 |
| 49 $Pccm$ | 28, 60 | 4, 2b | 2.73(3) and 2.82(2)/2.69(3) and 2.72(3) | 2.46, 4.59 |
| 46 $I2cm$ | 25, 62 | 2, 2 | 2.705(6)/2.767(6) | 2.50, 4.61 |
| 45 $Iba2$ | 22, 57 | 4, 2 | 2.71(3)/2.78(3) | 2.36, 4.46 |
| 33 $P2_1cn$ | 40, 119 | 4, 2 | 2.71(3)/2.77(4) | 2.26, 4.32 |
| 32 $Pba2$ | 44, 115 | 8, 4 | 2.78(6)/2.76(8)/2.67(8)/2.80(8) | 2.23, 4.31 |
| 30 $P2an$ | 42, 117 | 4, 4 | 2.73(3)/2.77(3)/2.68(3)/2.77(3) | 2.19, 4.23 |
| 29 $Pca2_1$ | 40, 119 | 4, 2 | 2.74(6)/2.76(6) | 2.12, 4.17 |
| 28 $P2cm$ | 50, 125 | 4, 2b | 2.67(4) and 2.74(4)/2.76(5) and 2.78(5) | 2.29, 4.34 |
| 27 $Pcc2$ | 44, 115 | 8, 2b | 2.76(9) and 2.78(9)/2.76(6) and 2.69(6) | 2.14, 4.20 |
| 26 $P2_1am$ | 48, 127 | 4, 4 | 2.69(3)/2.70(3)/2.86(2)/2.70(3) | 2.36, 4.42 |
| 23 $I222$ | 24, 56 | 4, 2b | 2.70(3) and 2.71(3)/2.75(3) | 2.43, 4.51 |
| 18 $P2_21_2$ | 42, 118 | 4, 2b | 2.67(3) and 2.74(3)/2.77(5) | 2.23, 4.28 |
| 16 $P222$ | 48, 112 | 8, 4b | 2.85(4) and 2.70(4)/2.78(6) and 2.75(6)/2.68(4) and 2.62(5)/2.78(6) and 2.75(6) | 2.22, 4.25 |

* Subgroup of space group 72 ($Ibam$).
* Different Cu — Cu distances within one or more dimer layers.

IV. DISCUSSION AND SUMMARY

We have investigated the low-temperature structural phase transition in BaCuSi$_2$O$_6$ by means of powder synchrotron x-ray and neutron diffraction and have determined the most probable average crystal structure of its LT phase. The proposed crystal structure model of the LT phase of BaCuSi$_2$O$_6$ has space group $Ibam$, and contains two individual Cu atom positions (with only one in the room-temperature structure). These two Cu atoms are forming two types of Cu — Cu dimers thus altering the most essential magnetic Cu — Cu exchange path lengths in a stacking manner along the $c$ axis. The interlayer Cu — Cu exchange distances are also becoming barely different at low temperature, forming in total two distinct but close interlayer Cu — Cu distances. In agreement with the previous study (Ref. [24]), we confirm the phase transition to be of first order, with a unit cell volume discontinuity of $\sim 1\%$ at the transition temperature, and a temperature hysteresis of $\sim 17.5$ K (the 50 : 50 phase weight proportions being achieved at $\sim 89.7$ K on cooling.
and at \( \sim 107.2 \text{K on heating} \). In the LT crystal structure, the layers with shorter Cu – Cu dimer distances (\( \sim 2.701 \text{Å at 13 K} \)) preserve the mutual rotation of the CuO\(_4\) coordination squares with respect to each other in the Cu – Cu dumbbells and the squarelike shapes of the (SiO\(_3\))\(_4\) molecules around them. This feature which is characteristic for the room-temperature structure is lost in the layers with longer Cu – Cu bonds (\( \sim 2.774 \text{Å at 13 K} \)); the coordination CuO\(_4\) squares in them unfold the mutual rotation and are aligned identically, and the (SiO\(_3\))\(_4\) molecules get strongly elongated along one of the \( a – b \) diagonals, forming a checkerboard pattern of their elongation directions. Thus, in the LT crystal structure of BaCuSi\(_2\)O\(_6\), the two distinct adjacent Cu\(_2\)(SiO\(_3\))\(_4\) layers with different Cu – Cu dimer distances and even different internal geometries are alternating in a sequential manner along the \( c \) axis. This finding corroborates the interpretation of the low-temperature INS data in terms of existence of two strongly inequivalent dimer layers in BaCuSi\(_2\)O\(_6\) with possible further complex modifications to one of them. The lower energy excitations reported in\(^5\) would correspond to the Cu\(_2\) – Cu\(_2\) dimer layers with shorter Cu – Cu distances, while the higher energy multimode excitations correspond to the Cu\(_1\) – Cu\(_1\) dimer layers with longer Cu – Cu distances. The incommensurate modulation of the crystal structure observed before in different studies did not hinder the structure determination, since as shown in Ref. \(^{24}\) the intensities of the satellite reflections are \( \sim 10^4 \) times weaker than that of the fundamental reflections, and thus they did not disturb our powder diffraction based average structure determination.

Here we want to conclude with a remark about the possibility of Dzyaloshinskii-Moriya (DM) interactions for BaCuSi\(_2\)O\(_6\). All three, HT, RT, and LT, structures of BaCuSi\(_2\)O\(_6\) are centrosymmetric. However, at RT there is no inversion center in the middle of the Cu – Cu dimers, as correctly pointed out by Ref. \(^{24}\). The same holds for LT Cu\(_2\) – Cu\(_2\) dimer layers with shorter Cu – Cu distances. In contrast to this, the LT Cu\(_1\) – Cu\(_1\) dimer layer with longer Cu – Cu distances has similarly to the HT \( I4/mmm \) structure the inversion symmetry in the middle of the Cu dimer and the intradimer DM coupling would be forbidden. In the real structure of BaCuSi\(_2\)O\(_6\), the incommensurate modulation may well remove this local symmetry and make DM interaction allowed again.

We note that the results presented here provide a structural model for the compound which justifies the interpretation of previous INS and NMR data by a number of groups\(^{5,19}\) in terms of two inequivalent dimer layers in BaCuSi\(_2\)O\(_6\) with further complex modifications to one of the layers that may partially relieve frustration. Furthermore, the detailed structure information provided here will be important input for the ongoing \( ab \) \( initio \) calculations of the exchange interactions in this fascinating material.

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