# Low-temperature structural phase transition and incommensurate lattice modulation in the spin-gap compound BaCuSi$_2$O$_6$

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Results of high-resolution x-ray diffraction experiments are presented for single crystals of the spin-gap compound BaCuSi$_2$O$_6$ in the temperature range from 16 to 300 K. The data show clear evidence of a transition from the room-temperature tetragonal phase into an incommensurately modulated orthorhombic structure below $\sim$100 K. This lattice modulation is characterized by a resolution-limited reduced wavevector $\mathbf{q}_{IC} = (0, 0.129 \pm 0.001, 0)$ (reciprocal lattice units) referred to the orthorhombic lattice, and its second and third harmonics. The phase transition is first order and exhibits considerable hysteresis. This observation implies that the spin Hamiltonian representing the system is more complex than originally thought.

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## I. INTRODUCTION

BaCuSi$_2$O$_6$ is a quasi-two-dimensional compound composed of copper silicate layers separated by Ba ions. Within the Cu$_2$Si$_4$O$_{12}$ layers, Cu$^{2+}$ ions are arranged in well-separated, vertical dimers.[1,2] Consistent with the dimerized structure, the material is observed to have a singlet ground state in a zero magnetic field, with a large gap to the lowest excited triplet states.[3] Magnetic fields in excess of $H_{c1}$ $\sim$ 23 T close the spin gap, such that cooling in a large applied field results in a state characterized by long-range magnetic order.[4] At $T=0$, a quantum critical point (QCP) at $H_{c1}$ separates the quantum paramagnetic regime from the ordered state. Recent experiments probing the critical exponent associated with the approach of the phase boundary toward the QCP indicate that it is possible to describe the phase transition in terms of Bose-Einstein condensation (BEC) of delocalized triplets down to the lowest measured temperatures of 30 mK.[5,6] Unfortunately, the large spin gap of this material currently precludes direct measurement of the magnetic structure in the ordered state. For this reason it is particularly important to have a detailed understanding of the low-temperature crystal structure in zero magnetic field, since this will have important consequences for the nature of the high-field magnetic phase transition.

To date, the crystal structure of BaCuSi$_2$O$_6$ has only been determined at room temperature and above. Sparta and Roth[2] have found evidence for a subtle structural phase transition at 610 K, from a high-temperature (HT) phase with $I4/mmm$ (No. 139) symmetry, to a room-temperature (RT) phase with $I4_1/acd$ (No. 142) symmetry (Fig. 1). However, recent heat capacity and susceptibility measurements indicate the presence of an additional first-order phase transition at approximately 100 K,[7] which is also likely structural in origin. In this Rapid Communication we present results of high-resolution x-ray diffraction experiments performed at the Advanced Photon Source (APS) on single crystals of BaCuSi$_2$O$_6$ from 16 to 300 K. We find clear evidence for a first-order structural phase transition at approximately 100 K

to a low-temperature (LT) crystal structure, characterized by an orthorhombic distortion of the RT tetragonal structure, and the appearance of an additional incommensurate lattice modulation. We discuss the origin of this effect and the consequences for the high-field ordered state.

## II. EXPERIMENTAL METHODS

Single crystal samples of BaCuSi$_2$O$_6$ were grown via a slow-cooling flux technique, as described elsewhere.[5] The crystals were well formed, and had a small mosaic spread of $\sim$0.02°. High-resolution x-ray diffraction experiments were performed on the X-Ray Operations and Research 1BM bending magnet beam line[8] at the APS, Argonne National Laboratory. This study was done with a focused beam of 20.016 keV x rays. A Si(111) analyzer crystal was used in
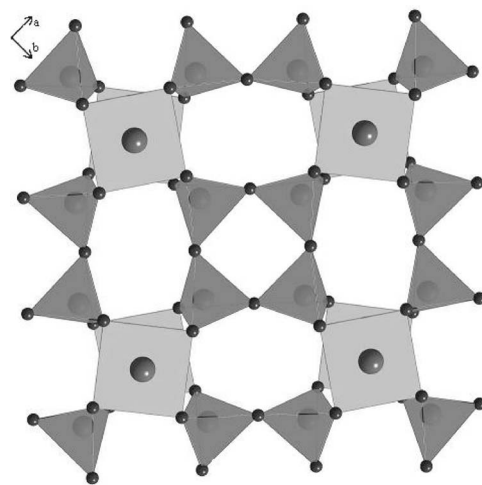


FIG. 1. Schematic of a copper silicate plane in the RT crystal structure of BaCuSi$_2$O$_6$ in the space group $I4_1/acd$ seen along the [0,0,1] direction. SiO$_4$ tetrahedra (dark polyhedra) combine to form a Si$_4$O$_{12}$ ring that is coordinated by pairs of vertically stacked CuO$_4$ groups (light planes).
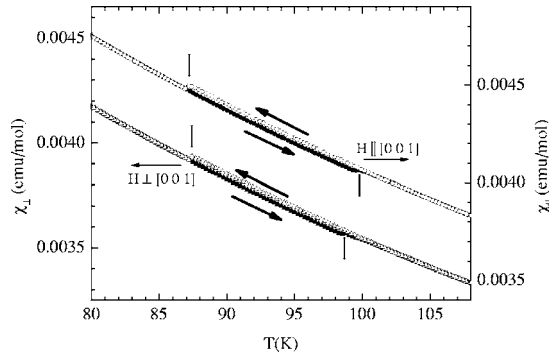
FIG. 2. Temperature dependence of the susceptibility of BaCuSi$_2$O$_6$ between 80 and 110 K, for an applied field of 5000 Oe oriented parallel and perpendicular to the crystalline *c* axis (circles and triangles, respectively). Data are shown for warming (solid symbols) and cooling cycles (open symbols), indicated by arrows. Jumps in susceptibility associated with the first-order phase transition are indicated by vertical lines.

order to suppress background and improve resolution. The sample was cooled using a closed-cycle refrigerator, with a base temperature of ~16 K. A Si-diode sensor was placed about 1 cm below the sample to measure its temperature.

Susceptibility measurements were made using a commercial Quantum Design MPMS5 superconducting quantum interference device (SQUID) magnetometer for a field of 5000 Oe aligned parallel and perpendicular to the crystalline *c* axis. Data were taken for both increasing and decreasing temperatures.

### III. RESULTS

The temperature dependence of the susceptibility of BaCuSi$_2$O$_6$ follows a form typical for weakly coupled spin dimer systems, and can be fit by a dimer model with a spin

gap of 4.45 meV, as has been previously reported by Sasago and co-workers.[3] Superimposed on this behavior, a weak jump in the susceptibility can be observed in the temperature range between 85 and 102 K (Fig. 2). The precise temperature at which the jump occurs depends on the thermal history of the sample, indicative of a first-order phase transition in this temperature range.

At room temperature, well above the transition observed in the susceptibility, charge Bragg peaks were observed consistent with the tetragonal structure previously reported by Sparta and Roth.[2] However, at 16 K the even-order $(h,0,0)$ Bragg peaks were observed to have split along the longitudinal direction as shown in Fig. 3. In addition, incommensurate (IC) satellite peaks appeared on either side of the split Bragg peaks. A careful set of measurements revealed that the splitting is consistent with transformation twins of an orthorhombic (or weakly monoclinic) lattice. These twins are rotated with respect to each other about the twofold *c* axis by ~89° as indicated in the inset to Fig. 3. From the splitting we found the degree of orthorhombicity defined as $\Delta_o = \frac{|a_o - b_o|}{(1/2)(a_o + b_o)} \approx 0.2\%$, where $a_o$ and $b_o$ are the orthorhombic lattice parameters ($a_o < b_o$; Fig. 4). The *c*-axis lattice parameter also exhibits a weak reduction (~0.5%) below the transition temperature. The IC peaks are characterized by a reduced wave vector $\mathbf{q}_{IC} = (0, 0.129 \pm 0.001, 0)$ (reciprocal lattice units) referred to the orthorhombic lattice, and its second and third harmonics. These IC peaks are resolution limited in all three directions implying a fully three-dimensionally ordered modulated structure for the LT phase. The intensity of the fundamental satellite is at least $10^4$ times weaker than that of the (0,8,0) Bragg peak.

The orthorhombic splitting and the intensity of the IC (0,8.129,0) peak were measured as a function of increasing temperature (Fig. 5). Both the splitting and the intensity of the IC peak remain nearly constant up to 103.8 K and disappear above that temperature. Within the resolution of our
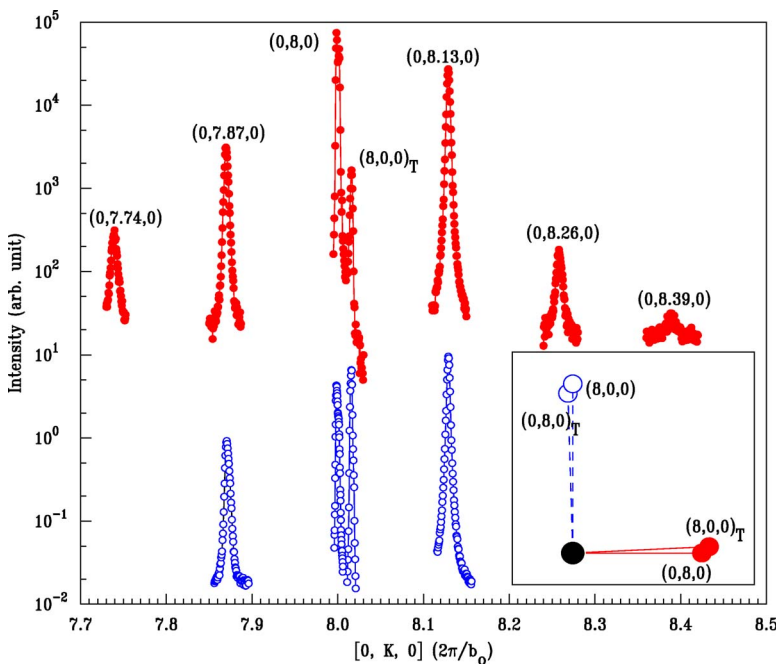


FIG. 3. (Color online) Reciprocal lattice scans (red solid circles) along the $\mathbf{b}^*$ axis showing the orthorhombic splitting of the (8,0,0) Bragg peak at 16 K. IC diffraction peaks and their higher harmonics are observed on either side of the Bragg point. Note that the corresponding peaks on two sides are equidistant from (0,8,0), not from $(8,0,0)_T$ of the twin partner. Schematic in the lower right corner illustrates split peaks from the twins. Scans along the orthogonal direction also reveal similar satellites (blue open circles; data were displaced down for clarity). In this case, the satellite peaks are associated with the $(0,8,0)_T$ Bragg peaks of the twin domain. Central Bragg peaks have been scaled down by a factor of ~$10^4$ to display on the same scale.
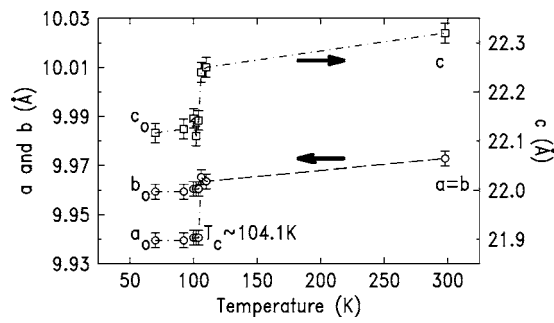
FIG. 4. The lattice parameters vs temperature on warming.

measurements we did not observe any change of $q_{IC}$ up to 103.8 K. An extensive search at 110 K confirmed the absence of both the orthorhombic splitting and the IC modulation. On cooling, both the splitting and the IC peaks reappear below ~91 K indicating hysteretic effects, similar to what is observed in the susceptibility (Fig. 2). The hysteresis of the transition is spectacularly demonstrated by the behavior of the IC peak with thermal cycling through the transition (inset, Fig. 5). On warming from 16 to 103.1 K, just below the transition, the peak is clearly observed (red circles). By raising the sample $T$ to 104.6 K, just above the transition, and subsequently cooling down to 100 K we were not able to recover the IC peak at 102.8 K (black squares). However, cooling down to 80 K and subsequent heating was sufficient to observe the peak up to 103 K on warming again (blue triangles). From such measurements we deduced that the transition is of first order, with transition temperatures ($T_c$) of 104.1±0.2 K and 91±1 K on warming and cooling, respectively. The observed transition width is remarkably sharp
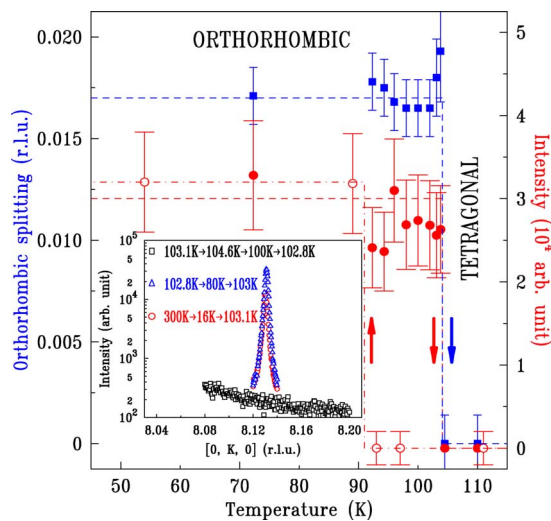


FIG. 5. (Color online) Temperature dependence of the orthorhombic splitting of the lattice (blue squares, left axis) and the intensity of fundamental IC modulation peak observed at (0,8.13,0) (red closed circles, right axis) measured on warming. The intensity of the IC satellite on cooling is shown as open red circles. Note the hysteresis. The inset displays scans through the satellite region for three different thermal cycling profiles through the transition, discussed in the main text. The data in the inset correspond to the final temperature of the given sequence of temperature set points.

$\left(\frac{\Delta T}{T_c} \sim 0.003\right)$, which is a measure of high quality and purity of the bulk single crystal. Values of $T_c$ differ slightly from those obtained from susceptibility measurements (Fig. 2) due to the differences in the cooling/warming rate, and the degree of undercooling/overheating, on approaching a temperature set point for these two experiments.

## IV. DISCUSSION

Low-$T$ IC modulated structures are not uncommon in silicates. Such modulations are usually due to a displacive phase transition of the lattice involving rotations of SiO$_4$ tetrahedra without substantial internal distortions of the tetrahedra themselves.[9–11] BaCuSi$_2$O$_6$ can be thought of as a "vierer" single ring cyclosilicate,[12] in which isolated Si$_4$O$_{12}$ rings (composed of four corner sharing SiO$_4$ tetrahedra) are linked by CuO$_4$ groups in the $ab$ plane, and separated by Ba cations between successive layers (Fig. 1). It is likely that SiO$_4$ tetrahedra in this compound rotate and twist as a rigid unit with respect to each other, causing a lattice modulation involving Ba and/or Cu atoms. The harmonic content (Fig. 3) implies a subtle squaring-up of the modulated structure, but a detailed description of the atomic displacements awaits a complete determination of the LT structure, which is beyond the scope of this initial survey.

The susceptibility data shown in Fig. 2 demonstrate that the change in crystal structure between the RT and LT phases of BaCuSi$_2$O$_6$ affects the magnetism of the system, albeit very weakly. These changes are presumably associated with subtle changes in the superexchange parameters coupling the spins in the lattice. Without a detailed structural model, it is difficult to predict how the intradimer ($J$) and interdimer ($J'$) exchange constants are affected, but we can anticipate that both will be modulated to some degree. We can, therefore, be fairly sure that the full spin Hamiltonian describing the system is slightly more complex than initially thought. We should note, however, that this structural study cannot provide an energy scale for the variations in the exchange parameters beyond suggesting that they are rather small, given that the intensity of the incommensurate satellite peaks is several orders of magnitude lower than the Bragg peaks associated with the average crystal structure.

The change in symmetry at the structural phase transition can also affect the magnetism via spin-orbit coupling. The HT ($I4/mmm$) structure has a center of inversion symmetry between the two Cu ions that comprise a dimer unit. However, the RT ($I4_1/acd$) and (presumably) LT structures do not, so additional terms $\vec{D} \cdot \vec{S}_1 \times \vec{S}_2$ (where $\vec{S}_1$ and $\vec{S}_2$ label spins in one dimer unit) due to antisymmetric Dzyaloshinski-Moriya (DM) exchange are not forbidden in the spin Hamiltonian for these phases. This is the lowest order effect by which spin-orbit coupling can introduce terms to the spin Hamiltonian that break axial U(1) symmetry [an essential prerequisite for BEC Ref. 13], because anisotropy in the $g$ tensor simply rescales the critical field $H_{c1} = \Delta/g\mu_B$. In the RT structure, copper dimers reside on axes of improper rotation $\bar{4}$ (an inversion tetrad), which within a single Cu$_2$Si$_4$O$_{12}$ sheet closely resembles an axis of fourfold symmetry. Ac-

cording to the standard symmetry rules for DM exchange,[14] the corresponding $\vec{D}$ vector for the RT phase would then point along the fourfold axis. Hence, for the RT structure it is anticipated that the $U(1)$ symmetry of the spin Hamiltonian will be preserved for magnetic fields aligned parallel to the crystalline $c$ axis. Without a complete structural model for the LT phase we have less insight to the symmetry of the dimers. However, we note that the structural distortion is slight, which implies that there will be minimal changes in the $\vec{D}$ vector.

In principle, the orthorhombicity of the LT structure can introduce an additional anisotropy to the spin Hamiltonian via a second-order effect associated with spin-orbit coupling. For a tetragonal structure, the $x$ and $y$ components of the interdimer exchange coupling $J'$ are perforce equal, but for an orthorhombic structure this does not have to be the case. The resulting symmetric anisotropy is quadratic in the spin-orbit interaction, (i.e., only appears in second-order corrections) and is therefore even smaller than any DM terms.

While the symmetry of the crystal lattice implies that the spin-orbit effects discribed above are possible, the magnitude of those terms must be measured by separate techniques. The observation of BEC critical scaling exponents[5,6] associated with the phase boundary imply that any $U(1)$ symmetry breaking terms that do enter the Hamiltonian must be on a significantly lower energy scale than the temperatures over which the magnetic ordering transition has been observed.

Finally, we note that the observation of an incommensurate structural modulation helps to understand the results of preliminary high-field NMR experiments on this material. In these experiments, Horvatić and co-workers have studied the NMR spectrum of $^{29}$Si nuclei at 0.04 K for fields just below $H_{c1}$ (23.4 T), and just above $H_{c1}$ (24.4 T).[15] Rather surprisingly, they find that the sharp NMR line below $H_{c1}$ is substantially broadened for fields above $H_{c1}$. Within a simple interpretation of the proposed triplet BEC, one would instead anticipate a splitting of the NMR lines corresponding to a doubling of the unit cell associated with the expected $(\pi/a, \pi/a)$ wave vector of the staggered magnetization.[6,15] The IC structural modulation provides a means to understand this observation without necessarily having to introduce a more complex magnetic structure. At a temperature of 0.04 K for fields below $H_{c1}$ there are essentially no thermally populated triplets, the uniform magnetization is zero, and the Si nuclei all see the same local magnetic field resulting in a relatively narrow NMR line. However, for fields above $H_{c1}$, there is a finite magnetization which causes a substantial Knight shift. Due to the incommensurate structure, each Si nucleus would see a slightly different magnetic field, broadening the NMR line shape. That is to say that the broadened NMR lines seen for fields above $H_{c1}$ do not necessarily correspond to an incomensurate *magnetic* structure, but more likely reflect the underlying incommensurate *crystal* structure of the LT phase. Further NMR experiments are called for to experimentally distinguish these two effects.

## V. CONCLUSIONS

In summary, our experiments have unambiguously shown the presence of a low-temperature structural phase transition in $BaCuSi_2O_6$, corresponding to an orthorhombic distortion of the RT $I4_1/acd$ structure and accompanied by an incommensurate modulation. The transition is first order, having a substantial hysteresis spanning approximately 80–105 K, depending on details of the warming or cooling cycles. The lower symmetry and incommensurate modulation of the LT phase imply that the spin Hamiltonian describing the magnetic properties of the system is more complex than previously thought. Electron spin resonance and inelastic neutron scattering experiments are currently in progress to determine the energy scale for additional relevant terms. Finally, the observation of an incommensurate structural modulation at low temperatures provides an important insight into the recent high-field NMR measurements for this compound.

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