The unusual 2-stage spin flop transition in BaCu$_2$Si$_2$O$_7$ is studied by single-crystal neutron diffraction. The magnetic structures of the various spin-flop phases are determined. The results appear to be inconsistent with the previously proposed theoretical explanation of the 2-stage transition.

I. INTRODUCTION

The quasi-one-dimensional (quasi-1D) $S = 1/2$ antiferromagnet BaCu$_2$Si$_2$O$_7$ is recognized as an almost ideal model material for studying exotic spin dynamics in weakly-interacting quantum spin chains. In a series of papers, we have demonstrated that in this compound it is possible to observe a separation between single-particle spin wave excitations, characteristic of a classical system with long-range magnetic order, and a gapped continuum of states that is a property of the quantum system with long-range magnetic order, and a gapped anisotropy gap of about 0.3 meV, corresponding to an anisotropy gap of about 0.3 meV, corresponding to an easy axis, and produce characteristic jumps in the magnetization curve. To date, the spin structure in the high-field phases has not been determined. However, in Ref. 5 it was suggested that upon going through the first transition, the spins “flop” into the $(a, b)$ crystallographic plane. The second transition was then described as an unusual spin rotation within the plane perpendicular to the field, and is somewhat similar to that recently found in K$_2$V$_3$O$_7$.

Based on an analysis of the high-field magnetization data, it was conjectured that the unusual second spin re-orientation in BaCu$_2$Si$_2$O$_7$ is a result of competition between Dzyaloshinskii-Moriya (DM) off-diagonal exchange interaction in the spin chains and isotropic exchange cou-
pling between the chains. In the present work we report the results of magnetic neutron diffraction studies of the various spin-flop states in BaCu$_2$Si$_2$O$_7$. We find the results to be inconsistent with the previously proposed model. It appears that inter-chain coupling dominates over DM interactions, and that the series of spin re-orientation transitions can not result from a competition between the two effects alone. Alternative mechanisms for the two-stage spin flop transition in BaCu$_2$Si$_2$O$_7$ are discussed.

II. EXPERIMENTAL

A $5 \times 5 \times 4$ mm$^3$ sample was mounted in a 6 T cryomagnet on the D23 lifting counter diffractometer at Institut Laue Langevin. The (0,0,1) axis was aligned parallel to the field direction. With 8 magnetic Cu$^{2+}$ per unit cell, in the ordered state all magnetic reflections coincide with nuclear ones. In addition, the ordered magnetic moment in BaCu$_2$Si$_2$O$_7$ is small, and detecting the magnetic contributions to Bragg intensities is rather difficult. The measurements were therefore performed in differential mode. At $H = 0$ T, 4 T (below $H_{c2}$) and 5 T (above $H_{c2}$) the diffractometer was consecutively positioned on each accessible Bragg reflection. Without moving any instrument motors, the peak intensity was measured first at 2 K and then again at 10 K. This measurement yielded the ratio of nuclear and magnetic scattering intensities. The absolute values of nuclear intensities were separately measured at 10 K in standard rocking scans. The rocking curves also provided an estimate of the background around each Bragg position. The measured integrated nuclear intensities, backgrounds, and peak intensity ratios were then used to estimate integrated magnetic intensities. In another experiment, the peak intensities of $\mathbf{Q} = (\mathbf{410})$, $(\mathbf{031})$ and $(\mathbf{051})$ reflections were monitored as a function of applied field in the range 0–5.5 T. Peak intensities measured in this fashion were assumed to be proportional to integrated intensities, with the normalization factor determined at $H = 0$, as described above.

III. RESULTS

Due to the strong in-chain coupling, any canting of neighboring spins away from a perfect antiferromagnetic alignment within each chain will be small and undetectable in our measurements. In analyzing the data, we could therefore safely rely on an approximation in which within each chain all spins are collinear. Inter-chain coupling is considerably weaker than the in-chain one, and is comparable in strength to the Zeeman energy associated with experimental fields. For this reason the relative orientation of staggered moments in neighboring chains could not be considered fixed, as it may actually vary with field. Since there are four chains within each unit cell of BaCu$_2$Si$_2$O$_7$, solving the magnetic structure at each field was reduced to determining the orientations of four spins, one from each chain, labeled as $\mathbf{S}_1$–$\mathbf{S}_4$ in Fig. 1.

A. Spin structure at zero applied field: Phase I

As a first step, we have verified that our new data collected at $H = 0$ are consistent with the structure previously reported in Ref. 3. The spins are parallel to the $c$-axis, with nearest neighbor spins along the $c$ and $b$ axes antiparallel to each other, and a parallel alignment of nearest neighbor spins along the $a$ axis, as shown in Fig. 1. This type of spin arrangement minimizes all inter-chain interaction energies that were independently measured using inelastic neutron scattering 4. Magnetic Bragg intensities calculated for this $c$-axis collinear state are in good agreement with those measured at $H = 0$ in the present work. This comparison is made in Table I.

B. Spin structure at $H = 4$ T: Phase II

The magnetic structure at $H = 4$ T was solved using a reverse Monte Carlo analysis, which unambiguously pointed to a planar state with all spins in the $(a,b)$ plane and a canting by an angle $\phi \approx 80^\circ$, as shown in Fig. 2 on the left. This structure is a slight distortion of a collinear one, with all spins parallel to the the $b$ axis, and the same relative alignment of spins in adjacent chains as at $H = 0$. A least-squares refinement of the canting angle and the ordered moment then yielded $\phi = 8(3)^\circ$, $m_0 = 0.18(2) \mu_B$, with a residual $\chi^2 \approx 2.4$. A comparison between measured and calculated magnetic intensities is given in Table I. Assuming $\phi = 90^\circ$ ($b$-axis collinear state), one can still get a reasonably good agreement with experiment, with $\chi^2 = 2.8$. Note that the magnetic

![Diagram](https://example.com/diagram.png)
structure of Phase II proposed in Ref. 1 (all spins parallel or antiparallel to the \(a\)-axis) is totally inconsistent with the present experiment, corresponding to \(\chi^2 = 64\), even when \(m_0\) is optimized to best fit the data.

### C. Spin structure at \(H = 5\) T: Phase III.

Fewer data points were collected at \(H = 5\) T than for the other two field values (see Table III). The best agreement with the data was obtained assuming a collinear structure with all spins pointing along the \(a\)-axis (Fig. 2, right), and the same relative alignment of spins in adjacent chains as at \(H = 0\). The refined value for the ordered moment is \(m_0 = 0.18(2) \mu_B\), and for this model \(\chi^2 = 4.5\). Again we note that the spin arrangement proposed in Ref. 1 for the high-field phase (all spins along the \(b\) axis and nearest-neighbor spins in the \(a\) direction aligned parallel to each other) is totally inconsistent with experiment, corresponding to \(\chi^2 = 158\).

### IV. FIELD DEPENDENCE.

The measured field dependencies of \((\overline{1}1\overline{1})\), \((0\overline{3}1)\) and \((0\overline{5}1)\) reflections are shown in Fig. 3. The data for Phases II and III were analyzed using the established models. The value of magnetic moment \(m_0\), as well as the canting angle \(\phi\) for Phase II were refined to best-fit the three intensities at each field. The results of the fit are shown in solid lines in Fig. 3, and the field dependence of the fit parameters is plotted in Fig. 4.

To obtain a good fit to the field dependencies measured in Phase I, an additional parameter had to be introduced to account for the large change in intensities just below the phase transition at \(H_{c1}\). By trial and error, it was found that the best way to reproduce this effect is to assume that the spin structure, as a whole, tilts towards the \(b\) axis (Fig. 5). In this model, when the direction of staggered moment passes through the \((0\overline{5}1)\) direction, the corresponding Bragg intensity shows a characteristic dip (arrow in Fig. 3a). This behavior is a result of
TABLE III: Measured magnetic intensities at $H = 5$ T in comparison to those calculated for the $a$-axis colinear state visualized in Fig. 2 (right).

| $h$ | $k$ | $l$ | $I_{\text{calc}}$ | $I_{\text{obs}}$ | $\sigma_{\text{obs}}$ | $\frac{I_{\text{obs}} - I_{\text{calc}}}{\sigma_{\text{obs}}}$ |
|-----|-----|-----|----------------------|-------------------|---------------------|----------------------------------|
| -4  | 1   | 0   | 0.845                | 0.110             | 0.890               | -0.826                           |
| -4  | -1  | -1  | 1.562                | 2.030             | 1.200               | 0.390                            |
| -4  | 1   | -1  | 1.562                | 4.570             | 1.470               | 2.046                            |
| -1  | -3  | -1  | 3.655                | 2.268             | 0.408               | -3.396                           |
| 0   | -5  | -1  | 49.258               | 54.301            | 1.672               | 3.016                            |
| -1  | -1  | -1  | 3.460                | 3.342             | 0.498               | -0.237                           |
| 0   | -3  | -1  | 68.598               | 61.640            | 2.690               | -2.587                           |
| -1  | 1   | -1  | 3.460                | 5.706             | 0.876               | 2.562                            |
| 1   | -3  | -1  | 3.655                | 2.200             | 0.725               | -2.008                           |
| -1  | -6  | -1  | 0.003                | 0.377             | 0.445               | 0.838                            |

$\chi^2 = 4.5$

$m_0 = 0.17(2) \mu_B$

FIG. 3: Measured field dependencies of several magnetic Bragg reflections in $\text{BaCu}_2\text{Si}_2\text{O}_7$ (symbols). The solid lines are a fit to the data at each field using the models described in the text. The arrows indicate intensity dips just below the phase transition at $H_{c1}$.

FIG. 4: Symbols: Measured field dependence of ordered moment (a), tilt angle $\alpha$ in Phase I (b) and canting angle $\phi$ in Phase II (c). The solid lines are a guide for the eye.

V. DISCUSSION

The data analysis described above was based on the known room-temperature crystal structure. The use of room-temperature structure factors to determine spin orientations at low temperatures may lead to systematic errors. Additional errors may be associated with measur-
ing magnetic intensities in the temperature-differential mode. Nevertheless, the results allow us to establish the main features of the three phases: 1) Nearest-neighbor spins within each chain remain almost anti-parallel to each other at all times. 2) The relative alignment of adjacent spins from neighboring chains does not deviate significantly from that at $H = 0$, with ferromagnetic spin alignment along $a$ and antiferromagnetic along $b$. Even in Phase II the canting is not very dramatic and vanishes just before the transition at $H_{c2}$. 3) The spins are oriented roughly along the $c$, $b$ and $a$ axis in phases I, II and III, respectively. 4) The ordered moment is only slightly different in each phase and is due to the suppression of 1D quantum spin fluctuations by the symmetry-breaking external field. The fact that $m_0$ remains practically constant when going through the phase transitions, means that in Phases II and III, $J_{1}$ does not change much and nearest-neighbor spins remain close to being parallel to one another along the $a$ axis and antiparallel along the $b$ and $c$ directions. This can be seen as an important self-consistency check for our determination of the spin orientations in the three phases. The overall gradual increase of the ordered moment as a function of $H$ seen in Fig. 3b is to be expected, and is due to the suppression of 1D quantum spin fluctuations by the symmetry-breaking external field. The slight suppression of $m_0$ observed in Phase II (Fig. 3b) is a result of the canted geometry, in which $|J_{\perp}|$ is reduced compared to that in Phase I. In the presence of canting ($\phi < 90^\circ$) the effective inter-chain coupling is given by $|J_{\perp}| = 2J_3 - (J_b + |J_a|)\cos(2\phi)$. In particular, just above $H_{c1}$, $\phi = 60^\circ$, and the drop in $m_0$ expected on going through the first phase transition due to the abrupt change in $|J_{\perp}|$ is about 23%. This value is in reasonable agreement with the observed $\approx 15\%$ effect.

Given the available data, the spin re-orientation at $H_{c1}$ can be described as a more or less conventional spin-flop transition, that one expects for a classical antiferromagnet in a magnetic field applied along the easy axis. In zero field, the easy-$c$-axis anisotropy energy is minimized when all spins are perpendicular to the $(a,b)$ plane. To take advantage of the Zeeman energy in applied fields, the spins have to align themselves perpendicular to $c$, to allow a canting of the rigid antiferromagnetic structure in the direction of $H$. Dzyaloshinskii-Moriya interactions and inter-chain coupling may modify the transition field and produce the small canting found in Phase II, but do not affect the basic physics of the effect. The fact that the transition appears to have a precursor, the spin structure tilting by an angle $\alpha$ at $H < H_{c1}$, may have several explanations. One possibility is that this phenomenon is result of an imperfect alignment of the external magnetic field relative to the $c$ axis of the crystal. Alternatively, it can be an intrinsic effect, due to the presence of Dzyaloshinskii-Moriya interaction, or to the existing structural canting of the local anisotropy axes of Cu$^{2+}$ relative to the $c$ axis. To fully resolve this problem, a careful determination of the magnetic structure just below and just above $H_{c1}$ will be required.

The second phase transition is much more unusual, since it involves a spin rotation in the plane perpendicular to $H$. It is clear that such behavior requires the presence of off-diagonal exchange interactions in the system. As recently observed in K$_2$V$_3$O$_8$, for example, a spin rotation around the field direction can be caused by a competition between DM interactions and magnetic anisotropy. This type of behavior is known since earlier studies of hematite. For BaCu$_2$Si$_2$O$_7$ though, a totally different explanation was proposed in Ref. 3 and the transition was attributed to a competition between DM coupling in the chains and isotropic inter-chain interactions, a mechanism similar to that previously discussed in relevance to the anomalous spin-flop behavior of La$_2$CuO$_4$.

The key argument of Ref. 3 is that the main components of the Dzyaloshinskii vector for the nearest-neighbor bond within the chains lie in the $(a,b)$ plane, and alternate sign from one bond to the next. In this case, DM interactions produce a weak-ferromagnetic canting of the spins within each chain even in zero applied field. In the presence of an external field, additional canting is due to Zeeman energy. The free energy of the system is minimized when the two canting effects are in the same direction. For this to be the case, nearest-neighbor spins along the $a$ axis have to be almost antiparallel to each other, since Dzyaloshinskii vectors in the adjacent chains are antiparallel as well. This preferred antiparallel orientation is in competition with ferromagnetic inter-chain coupling along the $a$ axis. In the model proposed in Ref. 3 the frustration is resolved in Phase II by having all spins aligned almost parallel to the Dzyaloshinskii vector (roughly along the $a$ axis), which practically eliminates the Dzyaloshinskii energy altogether, and the ferromagnetic inter-chain coupling energy along the $a$ axis is minimized. In Phase III the model predicts that the combination of DM and Zeeman energies wins over inter-chain interactions: the spins rotate to be almost parallel to the $b$ axis and cant in the direction of the applied field.
to minimize both energies. At the same time, nearest-neighbors along the $a$ axis become almost antiparallel, despite a ferromagnetic coupling in this direction.

The results presented above clearly demonstrate that the actual spin arrangements in BaCu$_2$Si$_2$O$_7$ in Phases II and III are totally different from those previously conjectured. In Ref. 1 it was emphasized that the Dzyaloshinskii vectors not being strictly parallel to the $a$ axis, and additional inter-chain interactions along the $(0, 1, 0)$ and $(1, 1, 0)$ directions being present, the critical field and the details of the spin structures may deviate from those predicted by the simplified model. However, even in the more general case, if the $H_{c2}$ transition in BaCu$_2$Si$_2$O$_7$ was indeed driven by a competition between DM interactions and isotropic inter-chain coupling, the energy of the latter would have to change abruptly upon going through the transition. The present data clearly show that this is not the case, since at $H_{c2}$ the spin structure rotates as a whole, and the relative spin orientations, and with them the inter-chain exchange energies, remain practically unchanged. It appears that inter-chain coupling dominates over DM interactions in all three phases. Because of the canting in Phase II, the energy of inter-chain interactions is actually better minimized in Phase III, rather than Phase II. This sequence is opposite to that emerging from the model proposed in Ref. 2.

We believe that at the present stage it is unwise to attempt a quantitative explanation of the phase transitions in BaCu$_2$Si$_2$O$_7$ based on some specific spin Hamiltonian. Too many parameters are involved to make such an analysis unambiguous. The energy scale of inter-chain interactions and $c$-axis anisotropy are indeed similar to that defined by transition fields. However, the Hamiltonian is expected to have other terms on the same energy scale, and these cannot be dismissed. In particular, measurements of the spin wave spectrum contain evidence of an in-plane anisotropy of the magnitude $\approx 0.15$ meV. This anisotropy is most likely due to the so-called Kaplan Schekhtman Entin-Wohlman Aharony (KSEA) interactions.[3] The KSEA term is a companion to DM interactions, and is an easy axis parallel to the Dzyaloshinskii vector. KSEA interactions are believed to be the driving force in the spin reorientation transition in K$_2$V$_3$O$_7$. The similarity of the behavior of the latter compound with that found in BaCu$_2$Si$_2$O$_7$ may indicate that anisotropy effects, and KSEA interactions in particular, could be responsible for the $H_{c2}$ transition in the silicate as well.

VI. CONCLUSION

In summary, the actual mechanism of the exotic two-stage spin flop transition in BaCu$_2$Si$_2$O$_7$ remains a mystery. What is clear, though, is that DM interactions and inter-chain exchange coupling alone can not sufficient to explain phenomenon. It appears more likely that both transitions in BaCu$_2$Si$_2$O$_7$ are caused by a competition between DM interactions and diagonal magnetic anisotropy effects, of which more needs to be learned.

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