Temperature-dependent spin gap and singlet ground state in 

\textbf{BaCuSi}_2\textbf{O}_6. 

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Abstract 

Bulk magnetic measurements and inelastic neutron scattering were used to investigate the spin-singlet ground state and magnetic gap excitations in \textbf{BaCuSi}_2\textbf{O}_6, a quasi-2-dimensional antiferromagnet with a bilayer structure. The results are well described by a model based on weakly interacting antiferromagnetic dimers. A strongly temperature-dependent dispersion in the gap modes was found. We suggest that the observed excitations are analogous to magneto-excitations in light rare-earth compounds, but are an intrinsic property of a simple Heisenberg Hamiltonian for the \( S = 1/2 \) magnetic bilayer.
Quantum-disordered low-dimensional (low-D) antiferromagnets (AF) have in the last two decades attracted a great deal of attention (see reference lists in Refs. [1–5]). Perhaps the simplest spin model that has a non-magnetic ground state is of zero dimensions. We refer here to a system composed of non-interacting dimers of \( S = 1/2 \) spins with AF Heisenberg intra-dimer exchange \( J \), the isolated-dimer (ID) model, where there is a finite energy gap \( \Delta = J \) separating the singlet \( S = 0 \) ground state from the excited \( S = 1 \) triplet. One of the first compounds to which this construct was found to be applicable was copper acetate that has been extensively studied by Güdel et al. [6]. More recently CaCuGe\(_2\)O\(_6\), was shown to possess many similar properties [7]. Extended networks of interacting dimers are currently an rapidly growing field in quantum magnetism. This increasing interest was triggered by recent studies of spin-ladders [8,9] and spin-bilayers [10], where inter- and intra-dimer spin-spin interactions are usually comparable in magnitude. It is therefore very unfortunate that the limit of weakly-coupled dimers could not be investigated experimentally in simple model systems like copper acetate or CaCuGe\(_2\)O\(_6\): in the former compound inter-dimer interactions are negligible, and only powder samples are currently available for the latter, which prevents a detailed study of the dispersion of the triplet excitations.

In this work we report our studies of the spin dynamics in BaCuSi\(_2\)O\(_6\). We show that the system is well described by a simple model of weakly-interacting AF dimers. Single-crystal inelastic neutron scattering is used to measure the finite dispersion in the dimer modes. The most intriguing and unexpected observation is that the dispersion is suppressed at temperatures higher or comparable to the characteristic gap energy. The physics of this behaviour could be understood through analogy with magnetic excitons in singlet-ground-state light rare earths. [11]

The tetragonal (space group \#14, \( a = 7.042 \) \( \text{Å} \), \( c = 11.133 \) \( \text{Å} \)) crystal structure of BaCuSi\(_2\)O\(_6\) has been investigated by Finger et al. [12] and is shown schematically in Fig. 1. Note that the structure is not that of previously studied CaCuGe\(_2\)O\(_6\) which has a zigzag-chain arrangement of Cu sites. In BaCuSi\(_2\)O\(_6\) the magnetic Cu\(^{2+}\) ions and the SiO\(_4\) tetrahedra are arranged in layers parallel to the (001) crystallographic plane. Within each Si-
O-Cu layer the Cu$^{2+}$ ions form a square-lattice \textit{bilayer} of $S = 1/2$ sites [Fig. 1(a)]. The nearest-neighbor in-plane Cu-Cu distance is large, 7.043 Å, equal to the $a$ lattice constant. The shortest Cu-Cu separation, 2.72 Å, is that between sites from complementary planes [Fig. 1(b)]. As we shall see, these Cu pairs form AF dimers. The Cu-Si-O bilayers are structurally separated from each other by planes composed of Ba$^{2+}$ ions.

Conventional AC-SQUID measurements on single-crystal samples reveal an activated behaviour of the magnetic susceptibility at $T \to 0$ that may be interpreted as a signature of a singlet ground state with a spin gap. No evidence of any magnetic phase transition was found. Raw data (not corrected for the effect of paramagnetic impurities) is plotted in symbols in Fig. 2(a). The observed $\chi(T)$ is in quantitative agreement with the theoretical prediction for the ID model with a singlet-triplet gap $\Delta = 4.1(0.03)$ meV [Fig. 2(a), solid lines].

The dimer ground state for BaCuSi$_2$O$_6$ was confirmed in inelastic neutron scattering experiments. These were performed on a $10 \times 4 \times 4$ mm$^3$ single-crystal sample grown using the floating-zone method. The measurements were done at the High Flux Beam reactor at Brookhaven National Laboratory on H8 and H7 3-axis spectrometers, using a neutron beam of fixed final energy $E_f = 14.7$ meV with a Pyrolitic Graphite (PG) filter positioned after the sample. PG (002) reflections were used for both monochromator and analyzer. The horizontal collimation setup was either $40' - 40' - 40' - 80'$ or $40' - 40' - 80' - 80'$. The sample was mounted with the $(h, 0, l)$ reciprocal-space plane coincident with the scattering plane of the spectrometer. The single crystal was of excellent quality, with a mosaic spread of $\approx 25'$. The measurements were done in the temperature range $3.5 - 150$ K, utilizing a closed-cycle refrigerator. Inelastic constant-$Q$ scans at $T = 3.5$ K revealed the presence of a gap excitation that appears around $(h\omega) \approx 4.5$ meV throughout the entire $(h, 0, l)$ plane [Fig. 2(b)]. At all temperatures between 3.5–150 K the inelastic peak is symmetric and has a practically $T$-independent energy width, slightly larger than the experimental resolution. The gap energy is in reasonably good agreement with that deduced from susceptibility data assuming the ID model.
To identify the particular pairs of Cu-spins that form the AF dimers we have analyzed the $Q$-dependence of the energy-integrated intensity in the gap excitations. Measurements at several wave vectors along $(h, 0, 1)$, $(h, 0, 1.25)$ and $(h, 0, 1.5)$ show that this intensity is independent of $h$, and only a gradual decrease is observed at large momentum transfers. The latter may be attributed entirely to effect of the Cu$^{2+}$ magnetic form factor $f(Q)$. In contrast, the energy-integrated intensity is strongly dependent on the $c^*$-component of the scattering vector, as shown in Fig. 3(a). A similar periodic intensity modulation was previously observed in copper-acetate [6]. The dynamic structure factor for isolated dimers can be obtained analytically:

$$S(Q, \omega) \propto \sin^2(Qd)|f(Q)|^2 \delta(h\omega - \Delta),$$  \hspace{1cm} (1)

where $2d$ is the vector connecting individual spins within a dimer. A fit of Eq. (1) to our $(0, 0, l)$ data on BaCuSi$_2$O$_6$ is shown in a solid line in Fig. 3(a). The analysis immediately provides us with the vector $d$: the dimers are oriented parallel to the $c$ axis with an intradimer spin-spin separation of 2.68(0.03) Å. This value coincides with the nearest-neighbor Cu-Cu distance in the crystal structure (2.73 Å). Note that at small $l$ the $(0.5, 0, l)$ data in Fig. 3(a) deviates from the theoretical curve. Indeed, preliminary experiments indicate that a very weak inelastic peak around $h\omega = 4$ meV is present in the entire $(h, k, 0)$ plane, where the dimer structure factor is zero. A finite cross-section at $l = 0$ represents dynamic spin correlations within the bilayers and thus a deviation from the isolated-dimer model. We are now in the process of further investigating this phenomenon. Below we concentrate only on the behaviour of the much stronger inelastic feature at $l \neq 0$ that, as we see, is easily understood within the framework of the dimer model.

Having established the dimerized nature of the ground state, we proceeded to study the dispersion in the dimer modes. No dispersion along the $c^*$ direction to within experimental errors. This is consistent with the layered quasi-2D structure of the material. In contrast, the dimer excitations have a finite bandwidth along the $a^*$ direction [Fig. 3(b), open circles for the 3.5 K data]. Note that the Brillouin zone for the magnetic gap excitations is the
same as for the crystal structure, and the spin fluctuations in BaCuSi$_2$O$_6$, unlike those in a
Neel antiferromagnet, retain the periodicity of the underlying lattice.

To analyze the observed dispersion relation we used a model Hamiltonian for a square-
lattice bilayer of $S = 1/2$ spins that has been investigated in connection to high-$T_c$
cuprate superconductors \[10\] and appears to be an appropriate description for the spin arrangement
in BaCuSi$_2$O$_6$. The bilayer Hamiltonian involves two Heisenberg AF exchange constants $J_1$
and $J_2$, between nearest neighbors from adjacent planes that form the bilayer and between
nearest neighbors within each plane, respectively \[10\]:

$$\hat{H} = J_1 \sum_i \hat{S}^{(1)}_i \hat{S}^{(2)}_i + J_2 \sum_{(i,j),\alpha} \hat{S}^{(\alpha)}_i \hat{S}^{(\alpha)}_j$$ \hspace{1cm} (2)

Here $i$ labels sites in a given plane, $i$ and $j$ are nearest neighbors in the same plane and
$\alpha = 1, 2$ label the two planes constituting the bilayer. The dispersion relation for (2) can be
easily derived from Eq. (2) in the limit $J_1 \ll J_2$. For $J_2 = 0$ the dimerized ground state is
exact. By treating the second term as a perturbation the following relation can be obtained:

$$\hbar \omega_{Q=(h,k,l)} = \Delta + 2 J_2 [\cos(h) + \cos(k)]$$ \hspace{1cm} (3)

The form (3) fits the data on BaCuSi$_2$O$_6$ very well, as shown in solid lines in Fig. 3(b). For $T = 3.5$ K the least-squares refinement yields $\Delta = 4.38(0.03)$ meV, $J_2 = 0.21(0.03)$ meV
and $J_1/J_2 \approx 20 \ll 1$. The physical picture for the finite-bandwidth modes are single-dimer
(local) excitations “hopping” from one site to another within the bilayer. In this respect
the magnetic excitations in BaCuSi$_2$O$_6$ are totally analogous to magneto-excitons in some
light rare-earth compounds \[11,13–15\]. The latter excitations are single-ion crystal-field (CF)
excitations “hopping” between rare earth centers by virtue of inter-site exchange interactions.
The difference is that in BaCuSi$_2$O$_6$ the localized excitations occur within a single AF dimer,
rather than on a single magnetic ion, and therefore have an intrinsic structure factor.

The most interesting results emerge from the study of the temperature-dependent behavior. Energy-integrated intensity was measured in constant-$Q$ scans as a function of
temperature in BaCuSi$_2$O$_6$ for $Q = (0,0,1.5)$ and $(0.5,0,1.5)$ [Fig 4(a)]. The intensity
starts to decrease with increasing $T$ and goes down by roughly a factor of four before leveling off above $T \approx 75$ K. This behaviour is consistent with the theoretical prediction \[7\] for the ID-model if one uses the previously obtained value $\Delta = 4.38$ meV [Fig 4(a), solid line]. What is obviously beyond the ID model and the first-order perturbation treatment of the Hamiltonian (3) is the \textit{temperature dependence of the excitation bandwidth}. At $T > 50$ K the magnitude of the dispersion along the $(h, 0, 1.5)$ direction is severely reduced compared to that at 3.5 K [Fig. 3(a), solid circles]. The suppression of dispersion is best illustrated in [Fig. 4(b)] that shows the temperature dependence of the excitation energy at $Q = (0, 0, 1.5)$ and $(0.5, 0, 1.5)$, where it is a minimum and maximum, respectively. The gaps for these two wave vectors converge with increasing $T$.

A physical understanding of the observed temperature dependence can be drawn from the previously mentioned analogy with magneto-excitons, where the dispersion in the magneto-exciton bands is also suppressed at high temperatures. A simplistic picture for this is that since no two excitations can simultaneously reside on one ion (dimer) at high temperatures, when the excited states are thermally populated, inter-site excitation hopping is inhibited and the bandwidth is reduced. The RPA (Random Phase Approximation) was very successful in describing the $T$-dependence of magnetic-excitons in Pr metal \[11,13,16\], PrBa$_2$Cu$_3$O$_7$ \[14\], and recently Pr$_2$BaNiO$_5$ \[13\]. Within this framework at a fixed momentum transfer the gap energy is given by \[13\]:

$$\Delta(T)^2 = \Delta_0^2 - \beta \Delta_0 R(T)$$

Here $\Delta_0$ is the gap for non-interacting ions (dimers). $\beta$ is a coefficient that contains the matrix element of the orbital momentum operator as well as the Fourier transform of the appropriate exchange integral. In our case $\beta$ must be proportional to $J_2$. $R(T)$ is a temperature-dependent renormalization factor, which is simply the difference in thermal populations of the ground and excited states. For singlet-to-triplet excitations we have:

$$R(T) = \frac{1 - \exp\left(-\frac{\Delta_0}{T}\right)}{1 + 3 \exp\left(-\frac{\Delta_0}{T}\right)}$$
The solid lines in [Fig. 4(b)] are results of a fit of Eqs. (4,5) to our data on BaCuSi$_2$O$_6$. Very good agreement for both wave vectors is obtained with $\Delta_0 = 4.22(0.02)$ meV and $\beta = -0.53(0.07)$ meV or $\beta = 1.15(0.07)$ meV for $\mathbf{Q} = (0, 0, 1.5)$ or $\mathbf{Q} = (0.5, 0, 1.5)$, respectively.

As we see, by substituting CF excitations for singlet-triplet AF dimer transitions the problem of weakly-interacting dimers may be mapped onto the problem of weakly-interacting singlet-ground-state rare-earth ions. In consequence the mathematical apparatus devised for magnetic excitons in rare earths describes the behaviour of BaCuSi$_2$O$_6$ very well. However, it is important to emphasize, that the microscopic physics of the two systems, BaCuSi$_2$O$_6$ and light rare-earths, is totally different. In the latter the singlet ground state and the single-ion CF excitations are result from relativistic spin-orbit interactions. In BaCuSi$_2$O$_6$ on the other hand, both the singlet ground state and the temperature-dependent dispersion are an \textit{intrinsic property of the Heisenberg Hamiltonian} for the particular coupling geometry and ratio of exchange constants.

In summary, we have observed temperature-dependent magneto-excitations in a $S = 1/2$ Heisenberg antiferromagnet.

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FIGURES

FIG. 1. Schematic view of the crystal structure of BaCuSi$_2$O$_6$: the Cu-Si-O layers parallel to $(a, b)$ plane [a] and and a projection along the $(0, 1, 0)$ direction [b]. Cu$^{2+}$ dimers are arranged in a square lattice to form a bilayer of $S = 1/2$ spins.

FIG. 2. (a) Magnetic susceptibility measured in a BaCuSi$_2$O$_6$ single crystal (symbols). The solid lines are theoretical curves calculated for the isolated-dimer model. (b) Example constant-$Q$ scans measured in BaCuSi$_2$O$_6$, showing the magnetic gap excitation at $\hbar \omega \approx 4.5$ meV. The solid lines are Gaussian fits.

FIG. 3. (a) Measured energy-integrated intensity of the inelastic peak in BaCuSi$_2$O$_6$ as a function of momentum transfer perpendicular to $(a, b)$ plane. The solid line represents the structure factor for an isolated dimer with $2d = 2.68$ Å. (b) Dispersion in the gap excitations measured along $(h, 0, 1.5)$. The solid lines represent fits to the data, as described in the text.

FIG. 4. (a) Measured temperature dependence of the energy-integrated intensity (a) and energy (b) of the gap excitations in BaCuSi$_2$O$_6$ at two different wave vectors. The solid lines are fits to the data described in the text.
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Abstract

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In contrast, the energy-integrated intensity is strongly dependent on the \(c^*\)-component of the scattering vector, as shown in Fig. 3(a). A similar periodic intensity modulation was previously observed in copper-acetate [6]. The dynamic structure factor for isolated dimers can be obtained analytically:

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S(Q, \omega) \propto \sin^2(Qd) |f(Q)|^2 \delta(\hbar \omega - \Delta),
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where \(2d\) is the vector connecting individual spins within a dimer. A fit of Eq. (1) to our \((0,0,l)\) data on BaCuSi\(_2\)O\(_6\) is shown in a solid line in Fig. 3(a). The analysis immediately provides us with the vector \(d\): the dimers are oriented parallel to the \(c\) axis with an intradimer spin-spin separation of 2.68(0.03) Å. This value coincides with the nearest-neighbor Cu-Cu distance in the crystal structure (2.73 Å). Note that at small \(l\) the \((0.5, 0, l)\) data in Fig. 3(a) deviates from the theoretical curve. Indeed, preliminary experiments indicate that a very weak inelastic peak around \(\hbar \omega = 4\) meV is present in the entire \((h, k, 0)\) plane, where the dimer structure factor is zero. A finite cross-section at \(l = 0\) represents dynamic spin correlations within the bilayers and thus a deviation from the isolated-dimer model. We are now in the process of further investigating this phenomenon. Below we concentrate only on the behaviour of the much stronger inelastic feature at \(l \neq 0\) that, as we see, is easily understood within the framework of the dimer model.

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To analyze the observed dispersion relation we used a model Hamiltonian for a square-lattice bilayer of $S = 1/2$ spins that has been investigated in connection to high-$T_c$ cuprate superconductors [10] and appears to be an appropriate description for the spin arrangement in BaCuSi$_2$O$_6$. The bilayer Hamiltonian involves two Heisenberg AF exchange constants $J_1$ and $J_2$, between nearest neighbors from adjacent planes that form the bilayer and between nearest neighbors within each plane, respectively [10]:

$$\hat{H} = J_1 \sum_i \hat{S}_i^{(1)} \hat{S}_i^{(2)} + J_2 \sum_{(i,j),\alpha} \hat{S}_i^{(\alpha)} \hat{S}_j^{(\alpha)}$$

(2)

Here $i$ labels sites in a given plane, $i$ and $j$ are nearest neighbors in the same plane and $\alpha = 1, 2$ label the two planes constituting the bilayer. The dispersion relation for (2) can be easily derived from Eq. (2) in the limit $J_1 \ll J_2$. For $J_2 = 0$ the dimerized ground state is exact. By treating the second term as a perturbation the following relation can be obtained:

$$\hbar \omega_{Q=(h,k,l)} = \Delta + 2J_2 [\cos(h) + \cos(k)]$$

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The form (3) fits the data on BaCuSi$_2$O$_6$ very well, as shown in solid lines in Fig. 3(b). For $T = 3.5$ K the least-squares refinement yields $\Delta = 4.38(0.03)$ meV, $J_2 = 0.21(0.03)$ meV and $J_1/J_2 \approx 20 \ll 1$. The physical picture for the finite-bandwidth modes are single-dimer (local) excitations “hopping” from one site to another within the bilayer. In this respect the magnetic excitations in BaCuSi$_2$O$_6$ are totally analogous to magneto-excitons in some light rare-earth compounds [11,13–15]. The latter excitations are single-ion crystal-field (CF) excitations “hopping” between rare earth centers by virtue of inter-site exchange interactions. The difference is that in BaCuSi$_2$O$_6$ the localized excitations occur within a single AF dimer, rather than on a single magnetic ion, and therefore have an intrinsic structure factor.

The most interesting results emerge from the study of the temperature-dependent behavior. Energy-integrated intensity was measured in constant-$Q$ scans as a function of temperature in BaCuSi$_2$O$_6$ for $Q = (0, 0, 1.5)$ and $(0.5, 0, 1.5)$ [Fig 4(a)]. The intensity
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A physical understanding of the observed temperature dependence can be drawn from the previously mentioned analogy with magneto-excitons, where the dispersion in the magneto-exciton bands is also suppressed at high temperatures. A simplistic picture for this is that since no two excitations can simultaneously reside on one ion (dimer) at high temperatures, when the excited states are thermally populated, inter-site excitation hopping is inhibited and the bandwidth is reduced. The RPA (Random Phase Approximation) was very successful in describing the $T$-dependence of magnetic-excitons in Pr metal [11,13,16], $\text{PrBa}_2\text{Cu}_3\text{O}_7$ [14], and recently $\text{Pr}_2\text{BaNiO}_5$ [15]. Within this framework at a fixed momentum transfer the gap energy is given by [13]:

$$\Delta(T)^2 = \Delta_0^2 - \beta \Delta_0 R(T)$$

(4)

Here $\Delta_0$ is the gap for non-interacting ions (dimers). $\beta$ is a coefficient that contains the matrix element of the orbital momentum operator as well as the Fourier transform of the appropriate exchange integral. In our case $\beta$ must be proportional to $J_2$. $R(T)$ is a temperature-dependent renormalization factor, which is simply the difference in thermal populations of the ground and excited states. For singlet-to-triplet excitations we have:

$$R(T) = \frac{1 - \exp \left( -\frac{\Delta_0}{T} \right)}{1 + 3 \exp \left( -\frac{\Delta_0}{T} \right)}$$

(5)
The solid lines in [Fig. 4(b)] are results of a fit of Eqs.(4,5) to our data on BaCuSi$_2$O$_6$. Very good agreement for both wave vectors is obtained with $\Delta_0 = 4.22(0.02)$ meV and $\beta = -0.53(0.07)$ meV or $\beta = 1.15(0.07)$ meV for $Q = (0,0,1.5)$ or $Q = (0.5,0,1.5)$, respectively.

As we see, by substituting CF excitations for singlet-triplet AF dimer transitions the problem of weakly-interacting dimers may be mapped onto the problem of weakly-interacting singlet-ground-state rare-earth ions. In consequence the mathematical apparatus devised for magnetic excitons in rare earths describes the behaviour of BaCuSi$_2$O$_6$ very well. However, it is important to emphasize, that the microscopic physics of the two systems, BaCuSi$_2$O$_6$ and light rare-earths, is totally different. In the latter the singlet ground state and the single-ion CF excitations are result from relativistic spin-orbit interactions. In BaCuSi$_2$O$_6$ on the other hand, both the singlet ground state and the temperature-dependent dispersion are an *intrinsic property of the Heisenberg Hamiltonian* for the particular coupling geometry and ratio of exchange constants.

In summary, we have observed temperature-dependend magneto-excitons in a $S = 1/2$ Heisenberg antiferromagnet.

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FIG. 1. Schematic view of the crystal structure of BaCuSi$_2$O$_6$: the Cu-Si-O layers parallel to ($a$, $b$) plane [a] and a projection along the (0, 1, 0) direction [b]. Cu$^{2+}$ dimers are arranged in a square lattice to form a bilayer of $S = 1/2$ spins.

FIG. 2. (a) Magnetic susceptibility measured in a BaCuSi$_2$O$_6$ single crystal (symbols). The solid lines are theoretical curves calculated for the isolated-dimer model. (b) Example constant-$Q$ scans measured in BaCuSi$_2$O$_6$, showing the magnetic gap excitation at $\hbar \omega \approx 4.5$ meV. The solid lines are Gaussian fits.

FIG. 3. (a) Measured energy-integrated intensity of the inelastic peak in BaCuSi$_2$O$_6$ as a function of momentum transfer perpendicular to ($a$, $b$) plane. The solid line represents the structure factor for an isolated dimer with $2d = 2.68$ Å. (b) Dispersion in the gap excitations measured along ($h$, 0, 1.5). The solid lines represent fits to the data, as described in the text.

FIG. 4. (a) Measured temperature dependence of the energy-integrated intensity (a) and energy (b) of the gap excitations in BaCuSi$_2$O$_6$ at two different wave vectors. The solid lines are fits to the data described in the text.
BaCuSi$_2$O$_6$ (a) 

\[ \chi \text{ (emu/g)} \]

\( \vec{H} \parallel \vec{c} \)

\( \vec{H} \perp \vec{c} \)

(b) 

BaCuSi$_2$O$_6$

Q=(0,0,1.5)

Sasago et al. Fig. 2
**Sasago et al. Fig. 3**

**Panel (a)**
- Sample: BaCuSi$_2$O$_6$
- Temperature: $T=3.5$ K
- Integrated Intensity vs. $l$ (r.l.u.)
- Data points for $Q=(0,0,1)$ and $Q=(0.5,0,1)$

**Panel (b)**
- Temperature: $T=3.5$ K, $T=50$ K
- Integrated Intensity vs. $E$ (meV) for $Q=(h,0,0,1.5)$
- Data points for $h$ (r.l.u.)

Comparison of data points and curves for different temperatures and wave vectors.
BaCuSi$_2$O$_6$ Figure 4 (b)

E (meV) vs. T (K)

Integrated intensity (a.u.) vs. T (K)

- $Q=(0.5,0,1.5)$
- $Q=(0,0,1.5)$

Sasago et al. Fig. 4