Temperature-dependent spin gap and singlet ground state in $BaCuSi_2O_6$

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Bulk magnetic measurements and inelastic neutron scattering were used to investigate the magnetic properties of $BaCuSi_2O_6$, a quasi-two-dimensional antiferromagnet with a square-lattice bilayer structure. The compound was shown to have a spin-singlet dimerized ground state with a gap $\Delta \approx 4.5$ meV in the magnetic excitation spectrum. The dispersion of the gap modes was measured and found to be temperature dependent and totally suppressed at temperatures higher than the characteristic gap energy. The observed excitations are analogous to magnetoexcitons in light rare-earth compounds, but are an intrinsic property of a simple Heisenberg Hamiltonian for the $S=1/2$ magnetic bilayer. The behavior is discussed in comparison to that of related systems, in particular, $Cs_3Cr_2Br_9$. [S0163-1829(97)02714-8]

I. INTRODUCTION

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 nonmagnetic ground state is of zero dimensions. We refer here to a system composed of noninteracting dimers of $S=1/2$ spins with an AF Heisenberg intradimer 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] Although the ID case in itself is simple to the point of not being very interesting, many new interesting phenomena emerge if finite inter-dimer interactions are present. In particular, the singlet-triplet gap excitations have a finite and strongly temperature-dependent dispersion in the interacting-dimer case. This behavior has been previously observed experimentally and analyzed theoretically by Leuenberger *et al.* for the Cr-dimer compound $Cs_3Cr_2Br_9$.[7,8]

The discovery of the spin-Peierls transition in $CuGeO_3$ (Refs. 4 and 9) and dimerized ground state in $CaCuGe_2O_6$ (Refs. 10 and 11) triggered the search for new singlet-ground-state compounds among copper germanates and silicates. In this work we have used bulk magnetic measurements and inelastic neutron scattering to investigate the properties of one of these species, namely $BaCuSi_2O_6$. The tetragonal (space group $I\bar{4}m2$, $a=7.042$ Å, $c=11.133$ Å) crystal structure of this material 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 $CaCuGe_2O_6$ which has a zigzag-chain arrangement of Cu sites. In $BaCuSi_2O_6$ 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 *bilayer* of $S=1/2$ sites [Fig. 1(a)]. The Cu-Si-O layers are structurally separated from each other by planes composed of Ba^{2+} ions. The nearest-neighbor in-plane Cu-Cu distance is large, 7.043 Å, equal to the a lattice constant. The shortest Cu-Cu separation, 2.73 Å, is that between sites from complementary planes [Fig. 1(b)].

The bilayer spin arrangement makes $BaCuSi_2O_6$ a very interesting compound, related to several important quantum spin systems. On the one hand, it can be considered as a two-dimensional (2D) version of the spin ladder, a model that is realized in several recently investigated singlet ground state materials.[5,13] On the other hand, the $S=1/2$ bilayer model has been invoked to explain the magnetic properties of such high-temperature superconductor- (HTSC) -related cuprates as underdoped $YBa_2Cu_3O_{6+x}$ and $YBaCu_4O_8$ (Ref. 14 and references therein). Notably, in all these compounds the intra-plane and in-plane interactions are comparable in magnitude. In the present work we show that in $BaCuSi_2O_6$, on the contrary, the interplane antiferromagnetic exchange interactions are dominant. As a result, the ground state is dimerized (spin singlet) and the spin dynamics is that of weakly coupled dimers. The gap excitations

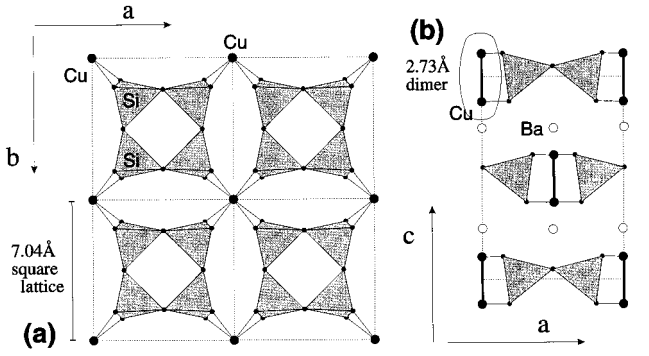

FIG. 1. Schematic view of the crystal structure of $BaCuSi_2O_6$: the Cu-Si-O layers parallel to the (a,b) plane (a) and a projection along the (0,1,0) direction (b). Cu^{2+} dimers are arranged in a square lattice to form a bilayer of $S=1/2$ spins.

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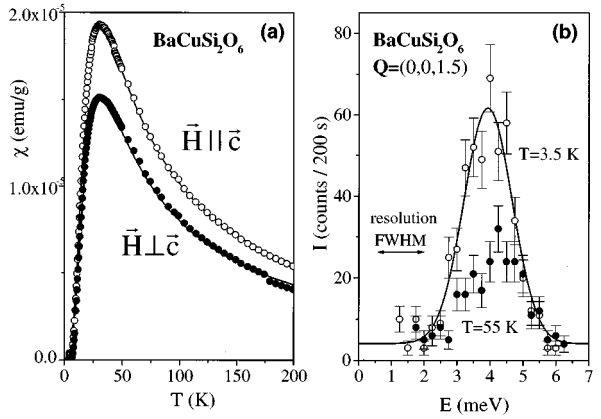

FIG. 2. (a) Magnetic susceptibility measured in a $BaCuSi_2O_6$ single crystal (symbols). The solid lines are theoretical curves calculated for the isolated-dimer model. (b) Example constant-Q scans measured in $BaCuSi_2O_6$, showing the magnetic gap excitation at $\hbar\omega \approx 4.5$ meV. The solid lines are Gaussian fits.

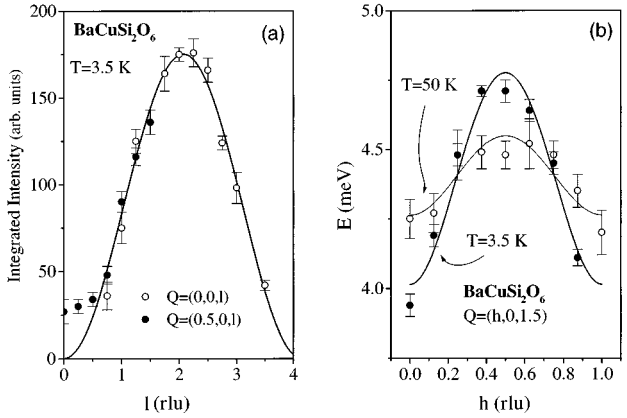

FIG. 3. Q dependence of the magnetic inelastic cross section measured in $BaCuSi_2O_6$: (a) Energy-integrated intensity of the inelastic peak as a function of momentum transfer perpendicular to the (a,b) plane. The solid line represents the structure factor for an isolated dimer with $2d = 2.68$ Å. (b) Dispersion in the gap excitations measured along $(h,0,1.5)$. The solid lines represent fits to the data, as described in the text.

have a finite temperature-dependent two-dimensional dispersion, and are similar to those found in $Cs_3Cr_2Br_9$.[7,8] The physics of this behavior is discussed by using an analogy with magnetic excitons in singlet-ground-state light rare earths.[15]

II. RESULTS

A. Magnetic susceptibility

Conventional AC-SQUID measurements on single-crystal samples reveal an activated behavior 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) are 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].

B. Inelastic neutron scattering

The dimer ground state for $BaCuSi_2O_6$ 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 the H8 and H7 three-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 $(h,0,l)$ zone 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 $\hbar\omega \approx 4.5$ meV throughout the entire $(h,0,l)$ plane [Fig. 2(b)]. At all temperatures between 3.5 and 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.

1. Structure factor

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:

$$S(\mathbf{Q},\omega) \propto \sin^2(\mathbf{Qd}) |f(Q)|^2 \delta(\hbar\omega - \Delta), \qquad (1)$$

where $2\mathbf{d}$ is the vector connecting individual spins within a dimer. Leuenberger *et al.* have derived a more general expression that is also valid in the case of interacting dimers.[8] As will be shown below, interdimer interactions are weak in $BaCuSi_2O_6$ and using the isolated-dimer form for the cross section is justified. A fit of Eq. (1) to our $(0,0,l)$ data on $BaCuSi_2O_6$ 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) deviate 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 should be zero. A finite cross section

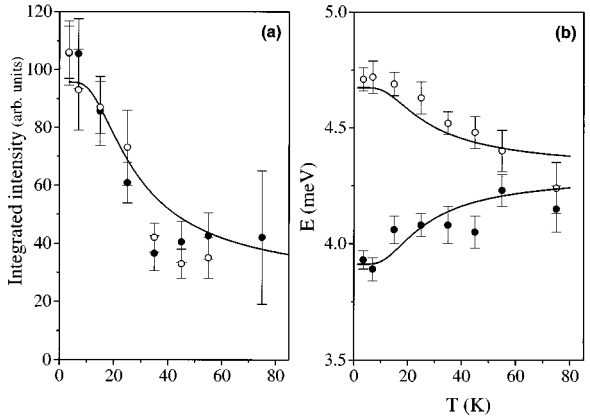

FIG. 4. Temperature dependence of the magnetic inelastic cross section measured in $BaCuSi_2O_6$: (a) Temperature dependence of the energy-integrated intensity (a) and energy (b) of the gap excitations in $BaCuSi_2O_6$ at two different wave vectors. The solid lines are fits to the data described in the text.

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 behavior of the much stronger inelastic feature at $l\neq 0$ that, as we see, is easily understood within the framework of the dimer model.

The temperature dependence of the energy-integrated intensity of the gap modes was measured in constant-Q scans for $\mathbf{Q}=(0,0,1.5)$ 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 behavior is consistent with the theoretical expectation for singlet-triplet dimer excitations if one uses the previously obtained value $\Delta=4.5$ meV [Fig 4(a), solid line].

2. Dispersion

Interdimer interactions result in a small yet significant dispersion in the dimer modes. To within experimental error we have not observed any dispersion along the c^* direction. 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), solid 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 $BaCuSi_2O_6$ retain the periodicity of the underlying lattice.

The magnitude of the dispersion was found to be strongly temperature dependent. At $T=50$ K the bandwidth along the $(h,0,1.5)$ direction is severely reduced compared to that at 3.5 K [Fig. 3(b), solid circles]. The suppression of dispersion is best illustrated in [Fig. 4(b)] that shows the temperature dependence of the excitation energy at $\mathbf{Q}=(0,0,1.5)$ 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.

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[14] and appears to be an appropriate description for the spin arrangement in $BaCuSi_2O_6$. We found, however, that including next-nearest-neighbor in-plane interactions, i.e., those along the diagonals of the square lattice, is essential. The bilayer Hamiltonian thus involves three Heisenberg exchange constants J_1 and J_2, and J_2', between nearest neighbors from adjacent planes that form the bilayer and between nearest and next-nearest neighbors within each plane, respectively:[14]

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

Here i labels sites in a given plane, $\langle ij\rangle$ and $\langle ij\rangle'$ are nearest and next-nearest neighbors in the same plane, respectively, and $\alpha=1,2$ label the two planes constituting the bilayer.

The physical picture for the dispersion in the dimer modes are single-dimer (local) excitations ''hopping'' from one site to another within the bilayer. In this respect the magnetic excitations in $BaCuSi_2O_6$ are totally analogous not only to those in $Cs_3Cr_2Br_6$, but also to magnetoexcitons in some light rare-earth compounds,[15–19] and even transition-metal systems.[20] The latter excitations are single-ion crystal-field (CF) excitations ''hopping'' between rare-earth centers by virtue of intersite exchange interactions. The difference is that in $BaCuSi_2O_6$ and $Cs_3Cr_2Br_6$ the localized excitations occur within a single AF dimer, rather than on a single magnetic ion, and therefore have an intrinsic structure factor. The RPA (random phase approximation) was very successful in describing the dispersion of magnetic excitons in Pr metal,[15,17,21] $PrBa_2Cu_3O_7$,[18] and recently Pr_2BaNiO_5.[19] For interacting dimers a very similar approach was developed by Leunberger *et al.*[8] in application to $Cs_3Cr_2Br_6$. In application to the bilayers in $BaCuSi_2O_6$ this RPA treatment yields

$$\omega_{\mathbf{Q}=(h,k,l)}=\sqrt{\Delta^2+\Delta J(\mathbf{Q})R(T)},$$

$$R(T)=n_0-n_1=\frac{1-\exp(-\Delta/T)}{1+3\exp(-\Delta/T)}, \tag{3}$$

$$J(\mathbf{Q})=2J_2[\cos(2\pi h)+\cos(2\pi k)]+2J_2'[\cos(2\pi\{h+k\})+\cos(2\pi\{h-k\})].$$

The temperature renormalization factor $R(T)$ was introduced by Houmann *et al.*,[16] and is simply the difference in thermal populations of the ground and excited states n_0 and n_1, respectively. Note that the measured dispersion is temperature independent at $\mathbf{Q}=(0.25,0,1.5)$. To account for this effect we thus have to assume $J_2=0$, i.e., the relavant in-plane exchange constant is J_2', that is, along the diagonals of the square lattice. The experimental data were analyzed by fitting Eq. (3) to the experimental data with two adjustable parameters, namely $J_1=\Delta$ and J_2'. For $T=3.5$ K the least-squares refinement yields a very good fit to the data with $J_1=\Delta=4.41(0.02)$ meV, $J_2=-0.19(0.03)$ meV, and $|J_1/J_2'|\approx 24\gg 1$. Moreover, by using parameter values obtained for $T=3.5$ K and Eq. (3) we can very accurately reproduce the dispersion measured at both $T=3.5$ K and $T=50$ K [Fig. 3(b), solid lines], as well as the entire experimental temperature dependence of the excitation energies at $\mathbf{Q}=(0,0,1.5)$ and $(0.5,0,1.5)$ [Fig. 4(b), solid lines].

A physical picture of the observed temperature dependence can be drawn from the previously mentioned analogy with magnetoexcitons, where the dispersion in the magnetoexciton bands is also suppressed at high temperatures. No two dimer (or CF) excitations can simultaneously reside on one site. At high temperatures ($T \gtrsim \Delta$) many dimers become thermally excited, and interfere with the propagation of other excitations. Intersite hopping is thus inhibited and the dispersion suppressed.

III. CONCLUDING REMARKS

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. Consequently, the mathematical apparatus devised for magnetic excitons in rare earths describes the behavior of $Cs_3Cr_2Br_6$ and $BaCuSi_2O_6$ very well. However, it is important to emphasize that the microscopic physics of the two systems, coupled dimers and light rare earths, is totally different. In the latter the singlet ground state and the single-ion CF excitations result from relativistic spin-orbit interactions. In $BaCuSi_2O_6$, on the other hand, both the singlet ground state and the temperature-dependent dispersion are an intrinsic property of the Heisenberg $S=1/2$ Hamiltonian for the particular coupling geometry and ratio of exchange constants.

In summary, we have observed a singlet ground state and a temperature-dependent two-dimensional dispersion of magneto-exciton-like gap modes in an $S=1/2$ Heisenberg square-lattice bilayer system. In future experiments we plan to investigate the effect of Zn and Sr doping on the magnetic properties of $BaCuSi_2O_6$ and study in-plane spin correlations in the pure material.

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