Spin-Triplet Excitons in the $S = \frac{1}{2}$ Gapped Antiferromagnet BaCuSi$_2$O$_6$: Electron Paramagnetic Resonance Studies

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BaCuSi$_2$O$_6$, a $S = \frac{1}{2}$ quantum antiferromagnet with a double-layer structure of Cu$^{2+}$ ions in a distorted planar-rectangular coordination and with a dimerized spin singlet ground state, is studied by means of the electron paramagnetic resonance technique. It is argued that multiple absorptions observed at low temperatures are intimately related to a thermally-activated spin-triplet exciton superstructure. Analysis of the angular dependence of exciton modes in BaCuSi$_2$O$_6$ allows us to accurately estimate anisotropy parameters. In addition, the temperature dependence of EPR intensity and linewidth is discussed.

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Electron paramagnetic resonance (EPR) is known as an extremely powerful tool for probing the magnetic excitation spectrum in exchange-coupled spin systems. A new theoretical approach for calculating low-temperature EPR parameters of $S = \frac{1}{2}$ AFM chains, which is based on bosonization and the standard Feynman-Dyson self-energy formalism, has been recently developed by Oslihawa and Affleck. The theory allows a precise calculation of the EPR parameters (such as linewidth and $g$ factor shift) and their dependence on temperature and magnetic field for uniform $S = \frac{1}{2}$ AFM chains and chains with staggered $g$ factor and the Dzyaloshinskii-Moriya interaction (so called sine-Gordon spin chains). The predictions were found in excellent agreement with experimental results.

In this article we continue studying EPR properties of low-dimensional (low-D) quantum spin systems. BaCuSi$_2$O$_6$ (barium copper cyclosilicate, also known as Han Purple Pigment) can be regarded as an almost ideal realization of the $S = \frac{1}{2}$ system of weakly-interacting spin dimers with the spin-singlet ground state and gapped excitation spectrum. By application of an external magnetic field the gap can be closed, creating a gas of interacting bosonic spin-triplet excitations (triplons). In BaCuSi$_2$O$_6$ this phenomenon can be effectively described in terms of the field-induced Bose-Einstein condensation of triplons. Here, we focus on another interesting phenomenon associated with interacting excited triplets but in the low-field quantum-disordered state, employing temperature as a tuning parameter. We argue, that a fine structure observed in low-temperature EPR spectra of BaCuSi$_2$O$_6$ is a fingerprint of triplet excitations (excitons), which are mobile at low temperatures and getting localized when temperature is increased. We show that anisotropic interactions in BaCuSi$_2$O$_6$ play a critical role significantly affecting the low-temperature EPR linewidth behavior.

BaCuSi$_2$O$_6$ crystallizes in the tetragonal non-centrosymmetric space group $I4/m$ ($Z = 4, a = 7.042$ Å, $c = 11.133$ Å). Magnetic Cu$^{2+}$ ions are arranged in layers with the $c$ axis perpendicular to the layers (Fig. 1). Within each layer Cu$^{2+}$ ions form a distorted planar-rectangular-coordination structure of $S = \frac{1}{2}$ sites (the O-Cu-O angle corresponding to bonds along the rectangular diagonal direction, 177.8°, deviates from that for an ideal planar configuration). The Cu$^{2+}$ ions from each two neighboring layers are coupled with each other, forming a two-dimensional dimer structure. The intradimer distance is relatively small, 2.743 Å, while the distance between dimers is 7.042 Å. The Cu bilayers are structurally separated from each other by planes of Ba$^{2+}$ ions. The quasi-2D nature of the interdimer interactions in BaCuSi$_2$O$_6$ has been confirmed by means of inelastic neu-
tron scattering [4], yielding \( J_1 \approx 51 \) K and \( J_2 \approx 2.2 \) K at temperature \( T = 3.5 \) K (where \( J_1 \) and \( J_2 \) are intra- and interdimer exchange coupling constants, respectively).

A well-defined single EPR line has been observed in BaCuSi\(_2\)O\(_6\) at room temperature. In Fig. 2 the angular dependences of the \( g \) factor and peak-to-peak EPR linewidth, \( \Delta B \), of this absorption in the \( ac \) plane, and in the \( ab \) plane, are shown. The line in Fig. 2 corresponds to a fit of the angular dependence of the EPR linewidth in the \( ac \) plane using the standard formula

\[
\Delta B / \Delta B_{\perp} = 1 + c \cos^2 \alpha,
\]

(1)

where \( \Delta B \) is the peak-to-peak linewidth and \( c \approx 0.54 \). Both the linewidth and \( g \) factor are anisotropic within the \( ac \) plane with a maximum along the \( c \) axis (\( \Delta B_c = 33.5 \pm 0.5 \) G, \( g_c = 2.306 \pm 0.003 \)), while being minimal and isotropic in the \( ab \) plane (\( \Delta B_{\perp} = 21.7 \pm 0.5 \) G, \( g_{\perp} = 2.050 \pm 0.003 \)). Since \( g_{\parallel} \neq 2 \) and \( g_{\perp} > g_{\parallel} \), the orbital singlet state \( d_{2z^2-\gamma^2} \) can be identified as the ground state, with electron-density maxima located in the basal \( ab \) plane.[5] Such a configuration suggests the absence of direct orbital overlaps between Cu sites from neighboring layers, revealing a strong superexchange mediating the Cu-Cu intradimer coupling.

In contrast to the room-temperature data, a very rich EPR spectrum has been observed in BaCuSi\(_2\)O\(_6\) at low temperatures (Fig. 4). The central line is split into four components labelled C1-4, which are clearly a sign of the hyperfine structure due to the \( I = 3/2 \) nuclear spin of unpaired doublet Cu\(^{2+} \) sites, caused by defects. A difference between resonance fields of absorptions B2 and B1 corresponds to a splitting between \( T_z = 0 \) and \( T_z = \pm 1 \) excited states (Fig. 4, inset). The absorption F (not shown in Fig. 4 but plotted in Fig. 4) is the so-called “half-field” resonance and corresponds to transitions between \( T_z = -1 \) and \( T_z = +1 \) levels. Since \( \Delta M_S = 2 \), these transitions are nominally forbidden, but become allowed by symmetry in certain situations, e.g., when wave functions from neighboring spin levels are mixed.[6]

Studying the angular dependence of the lines B1 and B2 allows an approximate estimate of the anisotropy parameter \( D \) using the expression

\[
B = B_0 \pm \frac{1}{2} \frac{D}{g \mu_B} \left( \frac{g^2}{g^2} \cos^2 \Theta - 1 \right),
\]

(2)

where \( g^2 = g_{\parallel}^2 \cos^2 \Theta + g_{\perp}^2 \sin^2 \Theta \). In our calculations we used the approach developed by Baranowski et al. [6],
which allows for a more accurate estimate of the zero-field splitting parameters for a fully anisotropic $g$ tensor and for every orientation of the field $B$. Results of the simulation are shown in Fig. 4 by lines. The best fit yields $g_{\perp} = 2.05$, $g_{||} = 2.31$ for the $g$ factor, and $D = 740$ G (0.1 K). Interestingly, the $g$ factors obtained from low-temperature data simulations are consistent with those obtained from room-temperature experiments.

Upon warming up the transitions B1 and B2 move towards each other and merge (Fig. 3), so that only one absorption line A can be resolved at temperatures higher than $\sim 12$ K. Spin-triplet excitations contribute to the EPR intensity, resulting in a pronounced peak in the temperature dependence at $\sim 40$ K (Fig. 5, circles). Since the interdimer exchange interaction in BaCuSi$_2$O$_6$ is significantly weaker than the intradimer coupling ($J_2 \ll J_1$), the isolated dimer model is used to fit the EPR data. The Boltzmann distribution is included to analyze the temperature dependence of the EPR signal and to determine the singlet-triplet energy gap $\Delta$. Normally, the EPR intensity is determined by a difference between populations of the lowest excited states, and at sufficiently low temperatures ($T \ll \Delta$) should be proportional to the number of thermally-activated triplet states. Thus, for the integrated absorption (and assuming a temperature independent size of the energy gap) we can write
\[ I(T) \sim \frac{\exp(-\Delta + g\mu_B B/k_B T) - \exp(-\Delta - g\mu_B B/k_B T)}{Z}. \]

where $\mu_B$ is the Bohr magneton, $k_B$ is the Boltzmann constant, $Z$ is the partition function for the singlet-triplet energy scheme, and $\Delta$ is the singlet-triplet gap. The best fit of the experimental data yields the mean energy gap of $\Delta = 53$ K, which is in excellent agreement with the data obtained from the neutron scattering measurements [4].

Since their relevancy to the understanding EPR properties of BaCuSi$_2$O$_6$, let us now discuss results of neutron scattering measurements [4] in more detail. It was observed that at low temperatures the interdimer coupling results in a relatively small but yet pronounced dispersion of triplet excitations along the layer direction. The physical picture of the dispersion of magnetic excitations in BaCuSi$_2$O$_6$ can be associated with single-dimer (local) excitations “hopping” from one site to another within the Cu$^{2+}$ bilayers. The delocalized, “excitonic” nature of spin-triplet excitations has been revealed, for instance, in some organic charge-transfer salts with spin singlet ground state [10]. It was shown that the exciton motion can be particularly prominent in low-D materials: it is very fast along one crystallographic direction and slow along other directions (1D propagation), or very fast within one crystallographic plane (2D propagation). The growing number of excitons causes pronounced changes in the dispersion of magnetic excitations in BaCuSi$_2$O$_6$.

As follows from neutron-scattering measurements [1], at $T \sim 50$ K the bandwidth along the in-plane direction is significantly reduced compared to that at 3.5 K, so that the dispersion of the triplet excitation becomes almost flat at high temperatures. Qualitatively the observed behavior can be described as following: at high temperatures excitons can not freely hop form one site to another (since most of the sites are already occupied), so that the dimer excitations have to reside on their own sites. Thus, triplets get localized, which manifests itself in the suppression of the excitation dispersion at high temperatures.

Let us now discuss the EPR results. As we saw above, the fine structure observed in the low-temperature regime can be nicely reproduced taking into account an anisotropy parameter $D = 0.1$ K, characterizing the excited triplet state. Upon warming up, the two peaks in the fine structure are getting closer to each other. At $T \sim 12$ K (depending on the orientation, i.e., the original splitting of the two lines) the fine structure can not be resolved any more, and a single line is observed. Upon further temperature increase, the EPR line is getting narrower (Fig. 5) until the linewidth becomes almost constant at temperatures higher than $T \sim 20$ K. All these phenomena are textbook examples of the temperature-activated exchange processes taking place between the particular dimers excited to the triplet state. As described e.g. in Ref. 11, in the slow-exchange regime (exchange frequency $\nu \ll |g\mu_B B[22 - B1]|$) the two lines corresponding to the individual $\Delta M_S = 1$ transitions get broadened upon raising the temperature, and start moving towards each other, while in the fast exchange regime ($g\mu_B B[22 - B1] \ll \nu$) the single averaged line gets narrowed with increasing temperature [12].

The nature of the exchange cannot be easily discerned from the EPR-detected effects alone. There are two possibilities, which can be termed “static exchange” and “motional exchange”. In the first case the triplet excitations are immobile, while in the second case they move...
in-plane, “bumping” into each other with a frequency dependent on the concentration of the excited dimers. Combining the EPR observations with those obtained from neutron scattering one can clearly decide that it is the “motional exchange” that takes place in the system up to about 20 K. Above that temperature most of the dimers are already excited into the triplet state, and the excitons become immobilized. In such a case, the “static exchange” takes over, which is clearly not thermally activated.

The angular dependence of the EPR linewidth in the fast exchange regime requires some consideration. If the anisotropy of the EPR spectrum as shown in Fig. 2 were related entirely to the underlying fine structure, then the linewidth minima should appear at the two crossover points in the slow-exchange spectra - as shown in Fig. 4 i.e., approximately 30° from the a axis. Since this is not the case, with the linewidth minimum appearing along the a axis, and the linewidth following Eq. 11 it means that the reasons for the linewidth anisotropy must be more complex. Generally speaking, the EPR linewidth in low-D spin systems can be affected by several factors, including symmetric term (anisotropic exchange and dipole-dipole interactions) and the Dzyaloshinskii-Moriya interaction (for most recent discussion, see for instance, Ref. [13]). Analysis of all these parameters in connection with the temperature dependence of the EPR line in BaCuSi$_2$O$_6$ can be a rather complex and challenging problem. It would be very interesting to study theoretically a contribution of excitons to the EPR linewidth, whose concentration and mobility are temperature dependent.

As shown, analyzing the angular dependence of exciton modes in BaCuSi$_2$O$_6$ allowed the accurate determination of the anisotropy parameter D. The described procedure might be of particular importance for studying a generic phase diagram predicted for anisotropic $S = \frac{1}{2}$ quantum chains (see, for instance, Ref. [19]), and can be applied for a large number of $S = \frac{1}{2}$ quantum antiferromagnets with the dimerized spin singlet ground state. A low-temperature fine structure similar to that in BaCuSi$_2$O$_6$, has been recently revealed in the $S = \frac{1}{2}$ dimer spin system VOHPO$_4$ · $\frac{1}{2}$H$_2$O [14]. A multiple-peak EPR fine structure, caused by a rather complex topology of magnetic interactions (there are at least two non-equal positions of Cu$^{2+}$ ions) has been observed [16] in the quasi-2D gapped spin system β-Sr$_2$Cu(BO$_3$)$_2$ [17]. In both cases the linewidth exhibited a temperature dependence, similar to that in BaCuSi$_2$O$_6$. Anisotropy effects revealed in BaCuSi$_2$O$_6$, can be also relevant to the low-temperature EPR line broadening observed in the low-D spin antiferromagnets CuGeO$_3$ [18] and α$'$-NaV$_2$O$_5$ [19].

In conclusion, resonance properties of BaCuSi$_2$O$_6$, a quasi-2D gapped antiferromagnet with dimerized spin singlet ground state, has been studied by means of X-band EPR technique. We argued that multiple absorptions observed in low-temperature EPR spectra were intimately related to a thermally-activated spin-triplet exciton superstructure. We demonstrated that the analysis of the angular dependence of exciton modes could be used as a powerful tool for accurate estimation of zero-field splittings within triplet states (and corresponding anisotropy parameters) in gapped $S = \frac{1}{2}$ quantum antiferromagnets with the dimerized spin singlet ground state. We hope that our experimental findings will stimulate a theoretical interest, which would make not only qualitative, but also quantitative interpretation of the temperature dependence of EPR parameters in BaCuSi$_2$O$_6$ and related materials possible.

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