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Spin-triplet excitons and anisotropy effects in the $S = \frac{1}{2}$ gapped antiferromagnet $BaCuSi_2O_6$ ☆

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Abstract

$BaCuSi_2O_6$ can be regarded as an almost ideal realization of an $S = \frac{1}{2}$ system of weakly interacting spin dimers with spin-singlet ground state and gapped excitation spectrum. We argue that the fine structure observed in low-temperature EPR spectra of $BaCuSi_2O_6$ is a fingerprint of triplet excitations (excitons). Analyzing the angular dependence of the exciton modes allows us to precisely calculate the zero-field splitting within the triplet states and, correspondingly, the anisotropy parameter, $D = 0.07\,cm^{-1}$. The proposed procedure can be applied for studying anisotropy effects in a large number of $S = \frac{1}{2}$ gapped quantum antiferromagnets with dimerized or alternating spin structure.

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A rich phase diagram has been recently predicted for anisotropic $S = \frac{1}{2}$ quantum chains [1]. Depending on the sign and value of the anisotropy parameter, and exchange couplings the systems can possess a dimer, long-range ordered antiferromagnetic, ferromagnetic, or even more exotic (such as "spin fluid") ground states. That is why the information on anisotropy constants in quantum spin systems is of crucial importance. In this article, we report on low-temperature electron paramagnetic resonance (EPR) properties of $BaCuSi_2O_6$ (barium copper cyclosilicate, also known as Han Purple Pigment), which can be regarded as a quasi-two-dimensional (2D) gapped system of interacting dimers [2]. By application of an external magnetic field the gap can be closed, creating a gas of interacting bosonic spin-triplet excitations (triplons). In $BaCuSi_2O_6$ this phenomenon can be effectively described in terms of the field-induced Bose–Einstein condensation of triplons [3]. Here, we focus on another interesting phenomenon associated with interacting excited triplets but in the low-field quantum-disordered state. It is argued that the EPR fine structure observed in $BaCuSi_2O_6$ at low temperatures is intimately related to spin-triplet excitons. We show that the analysis of the angular dependence of low-temperature magnetic excitations in gapped $S = \frac{1}{2}$ quantum systems can be used for an accurate estimate of the zero-field splitting within the excited triplet and, correspondingly, for the precise calculation of anisotropy parameters.

$BaCuSi_2O_6$ crystallizes in the tetragonal noncentrosymmetric space group $I\bar{4}m2$ ($Z = 4$, $a = 7.042\,Å$, $c = 11.133\,Å$) [4]. Magnetic Cu^{2+} ions are arranged in layers with the c-axis perpendicular to the layers. Two

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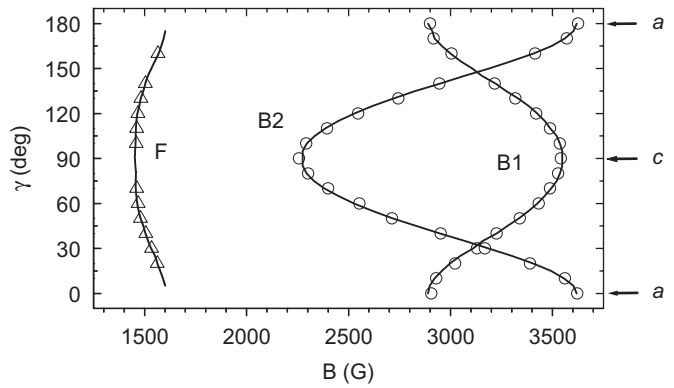

Fig. 1. Angular dependence of the EPR spectrum in $BaCuSi_2O_6$ in the *ac* plane, taken at a temperature of 6 K and frequency of 9.39 GHz. γ is the angle between the direction of the applied field and the *a*-axis. Triangles and circles correspond to experimental data, while lines correspond to simulation results (see text for details).

neighboring layers are coupled with each other, forming a 2D Cu^{2+} dimer structure. The intradimer distance is relatively small, 2.743 Å, while the distance between dimers is 7.042 Å. The quasi-2D nature of the interdimer interactions in $BaCuSi_2O_6$ has been confirmed by means of inelastic neutron scattering [2], yielding $J_1 \sim 51$ K and $J_2 \sim 2.2$ K at a temperature $T = 3.5$ K (where J_1 and J_2 are intra- and interdimer exchange coupling constants, respectively).

A single-peak EPR absorption has been observed in $BaCuSi_2O_6$ at room temperature. In contrast, a very rich EPR spectrum has been observed at low temperatures. Below 9 K the main EPR line is split into four components, which are clearly a sign of the hyperfine structure due to the $I = \frac{3}{2}$ nuclear spin of unpaired Cu^{2+} sites caused by defects and beyond the current consideration. In addition, three further lines have been observed. Two of them, denoted as B1 and B2 in Fig. 1, correspond to a splitting between $T_z = 0$ and $T_z = \pm 1$ excited states. The absorption F 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. To analyze the angular dependence of the low-temperature excitations in $BaCuSi_2O_6$ (Fig. 1), we used the approach developed by Baranowski et al. [5]. The approach allows an 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. 1 by lines. The best fit yields $g_\perp = 2.05$, $g_\parallel = 2.31$ for the g-factor, and $D = 0.07\,\mathrm{cm}^{-1}$ for the anisotropy parameter.

Upon warming up, the transitions B1 and B2 move towards each other and merge, so that only one absorption line can be resolved at temperatures above ~12 K. Upon further temperature increase, the EPR line is getting narrower until the linewidth becomes almost constant at temperatures higher than $T \approx 20$ 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. [6], in the slow-exchange regime (exchange frequency $\nu \ll g\mu_B|B2 - B1|$) 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 ($g\mu_B|B2 - B1| \ll \nu$) the single averaged line gets narrower with increasing temperature.

Spin-triplet excitations contribute to the EPR intensity, resulting in a distinct peak in the temperature dependence at ~40 K [7]. It is interesting to note that, on the other hand, the growing number of excitons appears to cause pronounced changes in the dispersion of the magnetic excitations in $BaCuSi_2O_6$. At $T \approx 50$ 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 [2]. Qualitatively the observed behavior can be described as following: at high-temperature excitons cannot hop freely from 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 and in the significant change of the EPR absorption. The delocalized, truly "excitonic" nature of low-temperature spin-triplet excitations has been revealed, for instance, in some organic charge-transfer salts with spin-singlet ground state [8].

In conclusion, low-temperature resonance properties of $BaCuSi_2O_6$, a quasi-2D gapped antiferromagnet with a 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 are intimately related to a thermally activated spin-triplet exciton superstructure. We demonstrated also that the analysis of the angular dependence of exciton modes can be used as a powerful tool for an accurate determination of zero-field splittings within triplet states (and corresponding anisotropy parameters) in gapped $S = \frac{1}{2}$ quantum antiferromagnets with dimerized spin-singlet ground state.

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