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Near critical behavior in the two-dimensional spin-gap system $SrCu_2(BO_3)_2$

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The temperature dependence of the powdered *X*-band ESR spectra has been measured in a two-dimensional spin-gap system $SrCu_2(BO_3)_2$ in the temperature range between 5 and 300 K. The spectra are composed of two overlapping components corresponding to isolated triplet excitations and correlated pairs of triplet excitations, respectively. The pairs of triplet excitations can propagate through the crystal resulting in the absence of any fine structure in the broad Lorentzian component contrary to the isolated triplet excitations which are almost completely localized. The temperature dependence of the broad Lorentzian linewidth indicates the importance of the antiferromagnetic correlations between the triplet excitations.

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I. INTRODUCTION

Two-dimensional (2D) systems that exhibit a spin gap have only recently received a lot of attention. The motivation has stemmed from the observations of a spin gap in high-T_C cuprates and the proposal of its potential importance for the occurrence of superconductivity in these materials. Two types of 2D spin gap systems were discussed so far. The first type are ladder systems, which represent an intermediate step from one-dimensional to two-dimensional spin systems.[1,2,3] The ground state of a ladder depends on the number of its legs. Systems with even number of legs (e.g., two-leg system $SrCu_2O_3$) have a spin-singlet ground state, while odd-number systems (e.g., three-leg system $Sr_4Cu_6O_{10}$) exhibit long-range order at low temperatures.[4] The singlet ground state proved to be extremely robust against the ladder-ladder interaction even when the interladder exchange interactions J'_C become sizeable up to $J'_C/J = 0.11$.[5]

The second type are dimer systems which exhibit spin-singlet ground state in 2D. A realization of this type is $SrCu_2(BO_3)_2$ system discovered recently.[6] In this system pairs of Cu^{2+} ($S = \frac{1}{2}$) ions are strongly antiferromagnetically coupled ($J = -100\,\mathrm{K}$ has been estimated from the high-temperature magnetic susceptibility behavior) and favor dimer spin-singlet states. However, each Cu^{2+} ion is also coupled to four next nearest (NN) Cu^{2+} sites. The NN coupling is very strong, i.e., $J' = 0.68J$.[7] The result is an interesting 2D network of Cu dimers, where each dimer is coupled to four neighboring dimers as shown in Fig. 1(a).[8] The unusual temperature dependence of the susceptibility [Fig. 1(b)] with a broad maximum at 20 K cannot be explained by simple dimer model.[6] A theoretical investigation of the two-dimensional Heisenberg model for $SrCu_2(BO_3)_2$ system was first conducted by Miyahara *et al.*[7] and several others followed later on.[9] They have found that this system is topologically equivalent to the one considered earlier by Shastry and Sutherland[10] which has the singlet state as an exact eigenstate. However, there exists a critical dimer-dimer exchange interaction $(J/J)_C = 0.69$,[7] above which the 2D dimer systems undergo a quantum phase transition from a spin-liquid singlet ground state to long-range ordered Néel state with increasing J'/J—a situation very reminiscent of the ladder systems.[5] The $SrCu_2(BO_3)_2$ system appears to be extremely close to this border $J'/J = 0.68(2)$.[7] The almost localized nature of the triplet excitations explains the appearance of $\frac{1}{4}$ and $\frac{1}{8}$ of the full Cu moment plateaus in the magnetization study.[6]

To our surprise the placement of $SrCu_2(BO_3)_2$ on the phase diagram (J'/J vs T) very near the border between the spin-liquid phase and long-range antiferromagnetically ordered state has not been discussed in detail. To address this problem it would be extremely interesting to investigate the temperature dependence of the spin correlation function in more detail. The electron spin resonance (ESR) proved to be very powerful technique for the detection of triplet excitations in low-dimensional solids.[11] It is expected that in $SrCu_2(BO_3)_2$ transitions within individual triplet excitations will be observed in *X*-band ESR, i.e., at the Larmor fre-

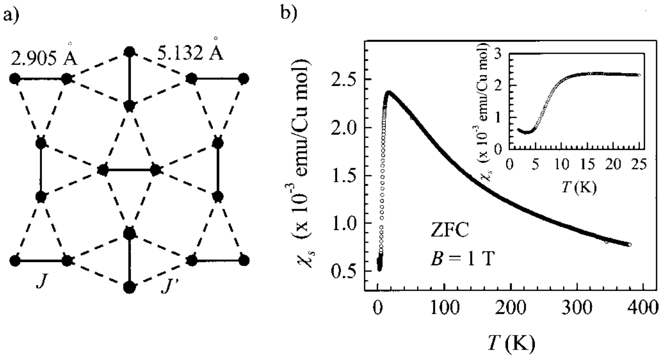

FIG. 1. (a) An illustration of the Cu^{2+} spin structure in $SrCu_2(BO_3)_2$, viewed down the [001] direction. Solid lines represent the nearest-neighbor bonds (J) and broken lines the coupling to four next-nearest neighbors (J'). The corresponding intradimer and interdimer distances are given in Å. (b) The temperature dependence of the zero-field cooled dc susceptibility for a $SrCu_2(BO_3)_2$ polycrystalline compound in a field of 1.0 T. Inset: shows a magnification of the low-temperature regime.

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quency of 9.38 GHz. Here we should mention that in a recent high-field ESR experiments (the resonant frequencies were varied between 95 and 788 GHz) Nojiri *et al.* already observed and identified direct singlet-triplet transitions.[12] Measuring the *X*-band ESR signal of powdered $SrCu_2(BO_3)_2$ between room temperature and 5 K we observed two different signals: a narrow one corresponding to about 3% of the total ESR signal and an intense broad one which we attribute to the two-dimensional network of dimers. The increase of the corresponding ESR linewidth with decreasing temperature is attributed to the proximity of the system to the quantum border between the spin-liquid phase and the antiferromagnetically long-range ordered phase.

II. EXPERIMENT

The fine blue $SrCu_2(BO_3)_2$ polycrystalline material was obtained by a solid state reaction of stoichiometric amounts of high-purity $Sr(NO_3)_2$, CuO, and B_2O_3 powders. The starting reagents were ground and mixed thoroughly, pressed at four tones into pellets and heated up in air at a rate of 5 °C/min to 450 °C for 12 h, then at elevated temperature of 850 °C for additional 12 h, followed by slow cooling to room temperature. After this initial stage the samples were ground, repelletized and fired in air at 850 °C for a period two weeks with three intermediate regrindings. Phase purity of the samples was confirmed by power x-ray diffraction using a Rikagu D/MAX-2000H rotating anode (12 kW) diffractometer equipped with a secondary graphite-crystal monochromator. dc magnetic susceptibility measurements between 1.8 and 400 K were carried out using a commercial Oxford Instruments MaglabExa susceptometer. The ESR experiment was performed on the conventional Bruker E580 FT/CW spectrometer in the *X* band at the resonant frequency $\nu_L = 9.38\,\mathrm{GHz}$. The spin susceptibility and the linewidth were measured in the temperature region between 5 and 300 K by continuous-wave operation. The temperature stability was better than ±0.1 K. The peak-to peak line width data were obtained from CW derivative spectra while the temperature dependence of the ESR intensity, which is proportional to the spin susceptibility χ_s, was deduced by a double integration of the measured derivative spectra. The corresponding value of molar spin susceptibility (in units emu/Cu mol) at room temperature was evaluated from the known mass of the $SrCu_2(BO_3)_2$ sample $m_s = 3.5\,\mathrm{mg}$ and the ESR intensity of the reference sample $CuSO_4 \cdot 5H_2O$ with a mass of 3.0 mg. The exact value of the molar spin susceptibility of the reference sample was calculated from the well-known Curie law.

III. RESULTS

A complex broad *X*-band ESR signal (Fig. 2) was observed in pure $SrCu_2(BO_3)_2$ powder sample between room temperature and 5 K. The signal was deconvoluted into two overlapping components: a broad Lorentzian and a narrow Gaussian component. The total intensity of the ESR signal corresponds to a spin susceptibility of 0.8×10^{-3} emu/Cu mol, e.g., similar to the value we obtained from the dc susceptibility measurements [Fig. 1(b)]. The narrow component represents only 3% of the total ESR intensity. In what follows we describe the temperature evolution of both components.

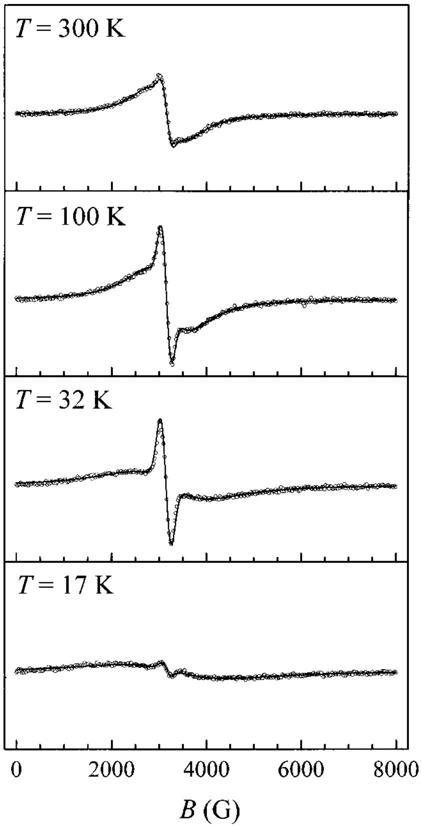

FIG. 2. A collection of CW derivative ESR spectra (open circles) for $SrCu_2(BO_3)_2$ with the amplitudes normalized to the $T = 300\,\mathrm{K}$ value. The smooth lines represent fits consisting of two components—a broad Lorentzian and a narrow Gaussian contributions.

Let us first discuss the narrow nearly Gaussian component. The temperature dependence of the intensity of the narrow component is shown in Fig. 3(a). The spin susceptibility gradually increases on cooling and reaches a maximum at 50 K. Below this temperature the signal rapidly decreases. The temperature dependence of the narrow component susceptibility could be fitted satisfactory using an $S = \frac{1}{2}$ isolated antiferromagnetically coupled dimer model[13] with a spin susceptibility

$$\chi_S^{\mathrm{dimer}} = \frac{Ng^2\mu_B^2}{k_B T} \frac{1}{3 + \exp[-2J/k_B T]}, \tag{1}$$

where N is the number of spins, μ_B the Bohr magneton, and J is the intradimer exchange coupling constant. The magnitude of the spin susceptibility corresponds to only 3% of the total number of Cu spins. Nevertheless it can give us important information regarding the strength of exchange interaction within the dimer as well as the expected linewidth for an isolated pair. The obtained exchange constant $J = -83 \pm 0.6\,\mathrm{K}$ is in the range between the originally reported value $J = -100\,\mathrm{K}$ and $J' = -68\,\mathrm{K}$ derived from susceptibility data.[6] On the other hand we note that the refined series

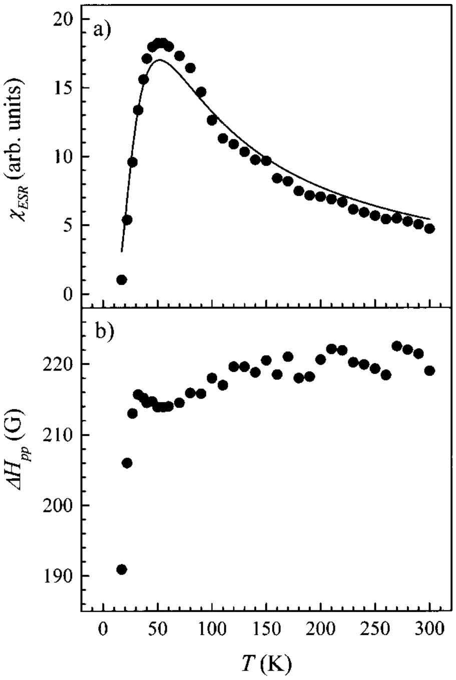

FIG. 3. (a) Temperature dependence of the intensity of the narrow Gaussian component of the $SrCu_2(BO_3)_2$ ESR spectra in the temperature range between 17 and 300 K. Solid line is a fit to an antiferromagnetically coupled dimer model [Eq. (1)], giving an exchange constant $J = -83 \pm 0.6\,K$. (b) Peak-to-peak line width of the Gaussian component in the same temperature interval.

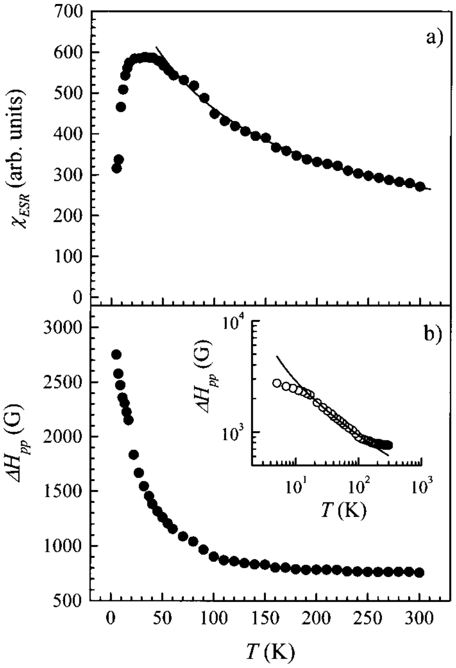

FIG. 4. (a) Temperature dependence of the intensity of the broad Lorentzian component of the $SrCu_2(BO_3)_2$ ESR spectra in the temperature range between 5 and 300 K. Solid line is a Curie-Weiss fit with a Curie-Weiss temperature $\theta' = -100\,K$. (b) Peak-to-peak linewidth of the Lorentzian component in the same temperature interval. The inset shows a log-log plot (circles), revealing a power-law behavior, given by Eq. (6) and a critical exponent $p = 0.51$ (solid line).

expansion[9] methods gave $J = -82\,K$, a value which is strikingly close to our observation. The linewidth of the narrow component is about 220 G and is nearly temperature independent [Fig. 3(b)] between 30 and 300 K. However, below 30 K the line suddenly starts to narrow. The observed line reveals some internal structure at low temperatures, which could be due to the dipolar splitting of the localized triplet excitation.

The broad Lorentzian component constitutes the major part of the ESR signal. The value of g factor as measured by ESR at room temperature is $g = 2.11$ which is the same as measured previously.[9] The temperature dependence of the ESR susceptibility of the Lorentzian component [Fig. 4(a)] mimics our dc susceptibility data [shown in Fig. 1(b)] as well as the one published earlier[6] with a very broad maximum at around 20 K and a rapid disappearance of the signal below this temperature. The room temperature ESR spin susceptibility value is $\chi_S = 0.8 \times 10^{-3}$ emu/Cu mol and is close to the value derived from dc susceptibility curve [Fig. 1(b)]. Analysis of the high-temperature ESR data in the range between 100 and 300 K, using a Curie-Weiss dependence $\chi_S \propto C/(T - \theta')$, gives a Curie-Weiss temperature of about -100 K which is comparable with $\theta' = -92.5\,K$ published earlier.[6,7] Below 50 K the susceptibility obeys an activated behavior $\chi_S \propto C' e^{-\Delta/T}$, which has already been observed and discussed previously.[6]

The temperature dependence of the linewidth of the broad Lorentzian line is shown in Fig. 4(b). First we note, that the line is rather broad, i.e., at room temperature the linewidth is 757 ± 3 G. This is nearly by the factor of 3 larger than the linewidth of the narrow component. This linewidth is also much broader than the ESR line of triplet excitations in the spin-Peierls system $CuGeO_3$.[11] At lower temperatures the observed ESR line broadens even more and the linewidth reaches a value of 2750 G at $T = 5$ K.

IV. DISCUSSION

In recent inelastic neutron scattering[14] and high-field ESR (Ref. 12) investigations basically two types of excitations were found at very low temperatures (i.e., at 1.6 K in ESR experiment). The first one has an energy gap of 3 meV, is almost dispersionless and corresponds to isolated triplet excitations. Interestingly, the second excitation lays only marginally higher, i.e., at 5 meV, and has been assigned to correlated pairs of triplet excitations with a much more pronounced dispersive behavior. Inelastic neutron scattering experiments found an additional excitation at 9 meV, which could be the excitation of more than two coupled triplet states. It is reasonable to discuss the origin of our ESR lines in terms of the above excitations. Although it is always possible that the narrow line with very small intensity corresponds to defects, the temperature dependence of the susceptibility and the magnitude of the extracted exchange constant J points to the suggestion that the observed line is in fact the isolated triplet excitation of the $SrCu_2(BO_3)_2$ 2D spin system. On the other hand, the broad line most probably corresponds to the correlated pairs of triplet excitations. In view to the fact that we measured the ESR at high temperatures and that each dimer has four nearest neighbor dimers, the possibility of finding two triplets together is quite substantial. The physical properties of the correlated triplets are hidden in the temperature dependence of the ESR linewidth.

To understand better the temperature dependence of the ESR linewidth, we first estimate the linewidth expected for a triplet state. There are only two important broadening contributions to the linewidth of a purely dimer system. More specifically, the contribution of the hyperfine interactions and that of the dipolar interactions between the excited triplet states. The hyperfine interaction between the unpaired electronic spin S and the Cu nuclear spins I_i $(I=\frac{3}{2})$ is

$$H_{\mathrm{hf}}=\sum_i \vec{I}_i\cdot A_i\cdot\vec{S}, \tag{2}$$

where A_i is the hyperfine coupling tensor. The hyperfine contribution to the total ESR linewidth for exchange coupled electronic spins has been calculated[15] in a high-temperature approximation for a one-dimensional antiferromagnet. The main result is that the hyperfine broadening of the ESR line is reduced when the antiferromagnetic exchange interactions are active—the process is called exchange narrowing. Typical values for components of the Cu hyperfine tensor A_i are $A_{\parallel}=210\,\mathrm{G}$ and $A_{\perp}=30\,\mathrm{G}$.[15] Thus whether or not the Cu hyperfine interactions are exchange averaged, their maximum contribution to the ESR linewidth is of the order of 200 G.

It is expected that in powdered $SrCu_2(BO_3)_2$ the dipolar interactions would strongly affect the ESR linewidth. To estimate the order of magnitude of the dipolar broadening we performed a calculation of the second moment using a standard formula for powdered samples[16]

$$M_2=\frac{3}{5}\gamma_e^4\hbar^2 S(S+1)\sum_{j,k} r_{j,k}^{-6}. \tag{3}$$

We assume that the most important interaction is the dipolar interaction between the excited triplet states (it has been shown that the intradimer dipolar interaction in the strong exchange limit leads to the effective zero field splitting term of the triplet state).[17] So in the first approximation we replaced each dimer with $S=1$ placed at the center of the dimers. Using the published lattice constants[8] we calculated the distances between the centers of the dimers r_{jk}. Considering up to nine nearest neighbors we estimated that with all dimers being in the triplet state $S=1$ the dipolar contribution to the linewidth would be of the order of $\Delta H^{dd}\approx 1000\,\mathrm{G}$. However, it is known that the true ground state is the singlet state with an energy gap between the ground state and the excited triplet state. Therefore, the system is in fact magnetically diluted and in this case the expected linewidth is even smaller than the above value. In such a case, the calculated linewidth must be multiplied with the spin concentration f, i.e., $\Delta H_{\mathrm{diluted}}=f\Delta H^{dd}$. At room temperature we estimated $f=e^{-\Delta/kT}/(1+e^{-\Delta/kT})=0.53$ so the dipolar contribution to the linewidth is of the order of 500 G.

Similarly as for the hyperfine interactions the antiferromagnetic exchange coupling between triplets would lead to exchange narrowing so the true contribution of the dipolar interactions to the total ESR linewidth should be even smaller than the above value. It is expected that at low temperatures the effect of exchange narrowing becomes less important due to reduced number of triplet excitations and as a result the dipolar contribution to the broadening should increase with decreasing temperature. We thus have two "competing" effects both arising from the temperature dependence of the number of triplet excitations: on one hand narrowing of the ESR line as the dipolar interactions become smaller and on the other broadening of the ESR line due to weaker exchange narrowing. However, the dipolar broadening is of the order of few hundred G as estimated above. We thus conclude that the hyperfine and the interdimer dipolar broadening mechanisms are not sufficient to explain the magnitude and the temperature dependence of the observed linewidth of the broad component, but they can explain the linewidth of the narrow component of the isolated triplet excitations. The difference between the two excitations lays in the fact that the triplet excitations assigned to the broad line are coupled together. We suggest that the magnetic broadening is responsible for the observed temperature dependence of the broad component.

Spin frustration in $SrCu_2(BO_3)_2$ system is highly important as suggested already in the original report.[6] In an attempt to rationalize further the above-mentioned behavior, one can examine the role of at least three possible mechanisms, including: critical broadening, stable magnetic point defects and anisotropy in the exchange interactions.

We note here that the temperature dependence of the linewidth of the broad ESR component is somewhat reminiscent of the one found in the two-dimensional triangular lattice antiferromagnets $HCrO_2$ and $LiCrO_2$.[18] There the inherent frustration effect causes a phase transition which is driven by the dissociation of the characteristic point-defects known as Z_2 vortices.[18,19] Z_2 vortices form bound pairs at low temperatures and begin to dissociate at a certain critical temperature T_{KM}. ESR linewidth above T_{KM} is expected to vary as

$$\Delta H\propto \exp(E_V/k_BT), \tag{4}$$

where E_V is the activation energy of the free Z_2 vortex. In the course of the analysis with this model, we did not succeed to obtain an accurate fit [Eq. (4)] of the temperature dependence of the linewidth of the broad ESR component in a large temperature interval. Due to possible similarities though, in the type of interactions between the intriguing 2D Cu^{2+} sublattice in the borate and that of the 2D triangular antiferromagnets, we can not at present disregard the assumption that Z_2 or similar vortices may play a role, since an exact theoretical description of the problem lacks for the $SrCu_2(BO_3)_2$ chemical system.

Let us now analyze the ESR data in terms of the ordinary critical broadening mechanism. The ESR linewidth, for strong antiferromagnetic fluctuations at q_0, is given by[20]

$$\Delta H \propto \frac{\langle S^Z_{q_0} S^Z_{-q_0} \rangle^2}{\Gamma_{q_0}} \xi^2, \tag{5}$$

where ξ is the inverse correlation length and Γ_{q_0} is the damping constant of $\langle S^Z_{q_0}(\tau) S^Z_{-q_0} \rangle$. For two-dimensional antiferromagnets $\Gamma_{q_0} \propto \xi$ and $\langle S^Z_q(\tau) S^Z_{-q} \rangle \propto \xi^{-2}$. It is thus reasonable to analyze the temperature dependence of the linewidth in terms of the reduced temperature $\varepsilon = (T - T_N)/T_N$, where T_N is a Néel temperature at which the sample would undergo a long-range antiferromagnetic ordering. The linewidth is thus expected to follow a power law

$$\Delta H \propto \varepsilon^{-p}. \tag{6}$$

In the inset of Fig. 4(b), the dependence of the ESR linewidth is shown as a function of the ε on a log-log scale. The data is reasonably fitted over a wide temperature range $(20\,\mathrm{K} \leqslant T \leqslant 100\,\mathrm{K})$ with $T_N = 2.3(2)$ K and critical exponent $p = 0.51(1)$. The fact that the power law fails to fit the data at lower temperatures (i.e., at $T < 20\,\mathrm{K}$) might be related to the significantly reduced number of triplet excitations at temperatures smaller than the spin gap, i.e., where the correlation length is expected to "shrink." We note here, that the value of the critical exponent is close to the one found in $MnTiO_3$ over a narrower temperature region, i.e., for $\varepsilon < 0.1$.[21] Although this analysis leads to a physically acceptable value for the critical exponent p, it is hard to believe that the critical region would extend up to $\varepsilon \approx 20$. However, as noted earlier, the $SrCu_2(BO_3)_2$ is situated extremely close to border between the spin-liquid state and long-ranged magnetically ordered state as $J'/J = 0.68$ is just marginally smaller than $(J'/J)_C = 0.69$.[7] In that case the strong antiferromagnetic fluctuations and the tendency towards the 3D Néel ordering of triplets can be present over a broader temperature range.

Finally we would like to mention that the anisotropic exchange coupling could ultimately lead to broadening of the ESR line similar to the one caused by the dipolar interactions. As discussed above for the case of dipolar broadening, a very complicated temperature dependence of the ESR linewidth is expected on cooling due to the temperature dependence of the number of triplet excitations. The same conclusion holds also for the antisymmetric Dzyaloshinsky-Moriya interaction, which has been suggested to be responsible for the direct singlet-triplet transitions observed by high-field ESR.[12] It has been argued that this is a likely reason for the broadening of the ESR line in the spin-Peierls system $CuGeO_3$ just below the transition temperature.[11] Thus, to explain the rather large linewidth of the observed broad ESR component, one must consider also the role of anisotropic exchange interactions. However, the analysis of the temperature dependence of their contribution to the ESR linewidth in $SrCu_2(BO_3)_2$ requires additional theoretical work.

At the end we would like to comment briefly on the observed line shape of the correlated pairs of triplet excitations. For the localized triplet excitation it is expected that the ESR line would be split due to the electron-electron dipolar interactions.[17] However, the absence of any dipolar fine structure of the broad ESR line and its Lorentzian shape can be explained in terms of motional averaging due to the propagation of pairs of triplet.[22]

In view of the fascinating theories for unusual quantum liquids involving doped chains, the example of the intriguing robustness[23] of the spin-liquid ground state in even-leg ladder compounds upon chemical substitution, prompts us to search for possible similarities in the ground state of the analogous quasi-2D $SrCu_2(BO_3)_2$ system. Although more experiments are needed to realize conducting borate compositions, when we attempted to dope $SrCu_2(BO_3)_2$ system so that aliovalent La^{3+} cations substitute for Sr^{2+} or isovalent Mg^{2+} for the Cu^{2+} sites neither an established superconducting state nor a suppressed spin-gap was observed.[24]

V. CONCLUSIONS

In conclusion we have measured the *X*-band ESR in a polycrystalline sample of the two-dimensional $SrCu_2(BO_3)_2$ spin system. Two distinct ESR signals have been identified: a narrow one which was assigned to the *isolated* triplets, and a broad one which corresponds to the *correlated* pairs of triplet excitations. The linewidth of the broad component shows a peculiar temperature dependence, which cannot be explained entirely in terms of hyperfine and dipolar broadening mechanisms influenced by the exchange narrowing. To understand the temperature dependence of the linewidth, one must consider also the effect of antiferromagnetic fluctuations between triplet excitations either in terms of critical broadening, or the presence of exchange anisotropy or in terms of a new type of bounded vortices similar to those found in triangular lattice antiferromagnets. Pairs of triplet excitations are strongly coupled together and the temperature dependence of the ESR linewidth suggests the importance of antiferromagnetic fluctuations and the tendency towards the Néel ordered state of triplet excitations. The absence of any fine structure in the broad ESR line can be explained in terms of propagation of pairs of triplet excitations. In further theoretical analysis two and more correlated triplet excitations should be considered both in terms of the interaction between pairs of triplet excitations as well as in terms of their (de)localization.

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