Collective Singlet Excitations and Evolution of Raman Spectral Weights in the 2D Spin Dimer Compound $SrCu_2(BO_3)_2$

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Raman light scattering of the two-dimensional quantum spin system $SrCu_2(BO_3)_2$ shows a rich structure in the magnetic excitation spectrum, including several well-defined bound state modes at low temperature, and a scattering continuum and quasielastic light scattering contributions at high temperature. The key to the understanding of the unique features of $SrCu_2(BO_3)_2$ is the presence of strong interactions between well-localized triplet excitations in the network of orthogonal spin dimers realized in this compound.

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Low-dimensional quantum spin systems with a quantum disordered ground state and a finite spin gap form a subject which is of both fundamental and applied interest to the physics community. This is due to the fascinating and diverse physics of the spin-liquid state, allowing one to address issues related to the nature of quasiparticle excitations and the role of strong interaction effects. It is known that a gapped singlet ground state is realized in one dimension (1D) in dimerized or frustrated spin chains, and in even-leg spin ladders. Of even greater interest is the existence of a gap in two-dimensional (2D) spin systems, because of its potential relevance for the description of high-temperature superconductivity. Unfortunately, only very few 2D systems, such as CaV_4O_9, have been investigated, in which the spin gap is relatively large and not caused by anisotropies. Recently, the compound $SrCu_2(BO_3)_2$ with a layered structure was identified as a 2D $S = 1/2$ Heisenberg system with a unique exchange topology [1,2] leading to an exact dimer ground state, thus providing the opportunity to study the excitation spectrum of such a model quantum many-body system.

$SrCu_2(BO_3)_2$ has a tetragonal unit cell (D_{2d}) with Cu^{2+} ions that carry a localized spin $S = 1/2$. The spins form dimers which consist of neighboring pairs of planar rectangular CuO_4 plaquettes with a Cu-Cu distance of 2.9 Å. The strength of the antiferromagnetic intradimer exchange coupling is estimated to be $J_1 = 100$ K [3]. The spin dimers are connected orthogonally by a triangular BO_3 unit. The distance between next-nearest Cu neighbors is 5.1 Å, and the interdimer exchange $J_2 \approx 68$ K [3]. The orthogonal arrangement of dimers thus represents a 2D frustrated quantum spin system [1,3]. A sketch of the Cu dimers is shown in the inset of Fig. 1(a). The ground state in this exchange topology depends critically on the ratio J_2/J_1 [3–5]. For small J_2 the system consists of isolated dimers and the ground state is a product of singlets, while for small J_1 the model can be mapped on a 2D square lattice of spins and a Néel-ordered state is expected. It has been shown that the critical ratio of coupling constants that separates a gapful and a gapless state is $J_2/J_1 = 0.7$ [3,4]. The experimental ratio of $J_2/J_1 \approx 0.68$ is just below this value, placing this material in the dimerized phase, close to the Néel boundary. Thermodynamic measurements support the existence of a dimer ground state and a spin gap of $\Delta = 34$ K [1,6]. The magnetic specific heat and susceptibility both show maxima ($T^{\chi}_{\max} = 15$ K, $T^{C_p}_{\max} = 8$ K) and a rapid decrease toward lower temperatures with exponential tails at $T \rightarrow 0$.

We have investigated the magnetic excitation spectrum of single crystals of $SrCu_2(BO_3)_2$ by Raman scattering experiments. At low temperatures ($T \ll \Delta$) we observe well-defined low-energy singlet modes which can be interpreted as collective bound state excitations of two and three elementary triplets. We demonstrate that the appearance of the collective modes reflects the strong triplet-triplet interactions present in the system. The spectral weight evolving for intermediate ($T \approx \Delta$) and high ($T > \Delta$) temperatures can be described by the temperature dependence of the magnetic susceptibility and the magnetic specific heat.

The samples were investigated in quasibackscattering geometry with light polarizations in the ab plane of the freshly cleaved crystal. The $(a'b')$ axes are rotated by 45° within this plane. The experiments used the $\lambda = 488$ nm excitation line of an Ar^+ ion laser and a laser fluence below 20 W/cm^2. The scattered light was analyzed using a XY-Dilor Raman spectrometer and a back-illuminated CCD detector. Measurements in a magnetic field were performed in 90° scattering geometry. In the analysis of our results the main emphasis has been on the role of interactions and their influence on the magnetic excitation

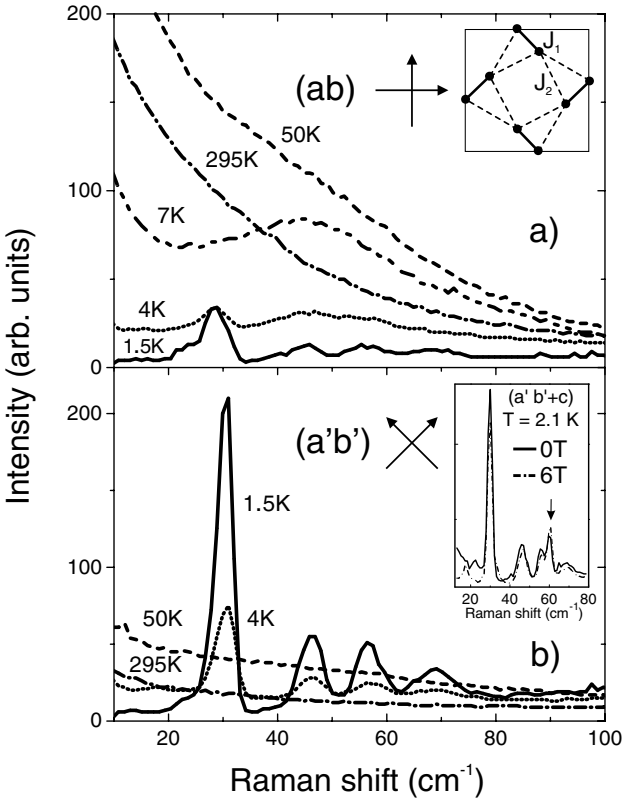

FIG. 1. Raman spectra of $SrCu_2(BO_3)_2$ in two scattering geometries. The upper inset shows Cu dimers of 1/4 of the unit cell formed by J_1 (full line) and J_2 (dashed line). The respective polarization (arrows) of incident and scattered light is given with respect to the crystallographic axes. The lower inset shows spectra for $B = 0$ (full line) and 6 T (dotted line) in $(a'b' + c)$ polarization. An additional A_g phonon is marked by an arrow.

spectrum. A detailed analysis of the phonon spectrum will be given elsewhere.

In the low-energy region with Raman shifts comparable to the triplet gap $\Delta = 24$ cm^{-1}, drastic changes and a large shift of spectral weight occur with decreasing temperature. This evolution leads finally to the appearance of several new modes. In Fig. 1 Raman spectra of $SrCu_2(BO_3)_2$ are shown to illustrate these effects at different temperatures and in two scattering configurations with light polarizations within the *ab* plane of the crystal. The spectra in the upper panel 1(a) present data in (ab):B_2 and the lower panel 1(b) shows data in $(a'b')$:B_1 scattering configuration. Symmetry components are denoted with respect to the D_{2d} point group using $b' = a + b$.

At low temperatures ($T \ll \Delta$) four well-defined modes with energies $E^S = 30$, 46, 56, and 70 cm^{-1} appear. The dominant intensity of these modes is observed in the $(a'b')$ scattering configuration. They neither split nor shift in an applied magnetic field up to 6 T as shown in the inset of Fig. 1(b) and therefore are assigned to spin singlets. The only effect of the magnetic field is observed as a shift of a weak intensity shoulder at 24 cm^{-1} toward lower frequencies. This signal corresponds to the elementary spin gap. At higher temperatures ($T \approx \Delta$) all modes are strongly damped. They are replaced by a continuum of scattering with a center of gravity near 50 cm^{-1} [Fig. 1(a), $T = 7$ K], corresponding roughly to the energy 2Δ. For even higher temperatures ($T > \Delta$) quasielastic scattering with a Lorentzian spectral function is detected. The latter two scattering intensities are observed in the (ab) scattering configuration.

To understand these dramatic changes of the Raman spectra with temperature we compare them with observations related to the triplet excitation spectrum and then map the temperature dependence of the scattering intensity onto the corresponding thermodynamic data, i.e., the magnetic susceptibility and the magnetic part of the specific heat. To gain a deeper insight into the structure of the spectrum we will also identify the interactions leading to the formation of singlet bound states in the relevant Heisenberg model at $T = 0$, and present estimates for their binding energies.

Recent ESR [7] and neutron scattering investigations [8] on $SrCu_2(BO_3)_2$ at low temperatures observed triplet excitations with a spin gap of $\Delta = 34$ K. This triplet branch has a very small dispersion of only 2 K pointing to extremely localized excitations [4]. In addition, a second triplet branch $\Delta' = 55$ K with a larger dispersion of 17 K was observed. This branch can be interpreted as a triplet bound state of two elementary triplets (see discussion below). Frustration due to the interdimer coupling J_2 can lead to the reduction of the ratio $\Delta'/\Delta = 1.62$ below 2 (corresponding to noninteracting magnons) [8].

The four modes that we observe in Raman scattering in $SrCu_2(BO_3)_2$ for $T \ll \Delta$ are clearly related in energy and temperature scale to the spin gap of the compound. A phonon origin of these modes can be ruled out due to their temperature dependence and the nonexistence of a structural phase transition below room temperature. On the other hand, in low-dimensional spin systems with strong triplet-triplet interactions, well-defined modes can appear below the scattering continuum [9–11]. In this case the light scattering process is better described as spin conserving ($\Delta S = 0$) scattering on singlet bound states. Such states composed of two elementary triplets have been observed, e.g., in the low-temperature dimerized phases of $CuGeO_3$ and NaV_2O_5 [12–14].

To illustrate the mechanism of bound state formation at $T = 0$ in the 2D Heisenberg model $H = \Sigma_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$ with $J_{ij} > 0$ defined in the inset of Fig. 1(a) (the Shastry-Sutherland model [15]), we have derived the effective bosonic representation in terms of triplets ($\mathbf{t}_i^\dagger$), excited above the singlets, formed on the stronger (J_1) bonds:

$$H = J_1 \sum_i \mathbf{t}_i^\dagger \cdot \mathbf{t}_i + V \sum_{\langle i,j \rangle} (\mathbf{t}_i^\dagger \times \mathbf{t}_i) \cdot (\mathbf{t}_j^\dagger \times \mathbf{t}_j) + \sum_{i \in A} \{ i\Gamma (\mathbf{t}_i^\dagger \times \mathbf{t}_i) \cdot (\mathbf{t}_{i+\hat{x}}^\dagger - \mathbf{t}_{i-\hat{x}}^\dagger + \text{H.c.}) \} + \sum_{i \in B} \{ \hat{x} \rightarrow \hat{y} \}, \quad (1)$$

where $V = -\Gamma = -J_2/2$. The site indices run over the square lattice formed by the dimers (singlet pairs of

spins connected by J_1 bonds), and $\langle i, j\rangle$ stands for nearest neighbors, while sublattice $A(B)$ is formed by the vertical (horizontal) dimers. An important feature of Eq. (1) is the absence of quantum fluctuations (i.e., $\mathbf{t}_i^\dagger \cdot \mathbf{t}_j^\dagger$ terms), reflecting the fact that the ground state is an exact product of singlets. The triplet excitations would have been completely localized in the absence of the Γ term in Eq. (1), and hopping appears only in order $(\Gamma/J_1)^6 \sim (J_2/J_1)^6$, leading to a small bandwidth compared to the gap [3,4].

Next we present estimates for the energies of the collective, *two-particle excitations.* The zero-momentum two-magnon bound state with $S = 0$, constructed by exciting two triplets, has the form $|\Psi^S\rangle = \sum_{i,j} \psi_{i,j}^S \mathbf{t}_i^\dagger \cdot \mathbf{t}_j^\dagger |0\rangle$. Starting from the limit $J_2/J_1 \ll 1$, the dominant contribution to binding comes from the two-particle interaction [V term in Eq. (1)], with corrections of order $(J_2/J_1)^2$ and higher. This interaction provides an effective attraction between two triplets. Assuming the triplets are localized, the binding problem can be solved exactly, and the singlet binding energy defined as $\epsilon^S = 2\Delta - E_2^S$ is $\epsilon^S = Z^2 J_2$. Here E_2^S is the energy of the singlet bound state, and we have estimated the renormalization factor Z by evaluating the appropriate lowest order diagrams to be $Z \approx 0.75$ at $J_2/J_1 = 0.65$. We have found, by comparing neutron scattering data for the one-particle dispersion from [8] with the dispersion obtained by high-order perturbative expansions [4] that the ratio $J_2/J_1 = 0.65$ is consistent with the experimental results. Indeed, for this ratio the theoretical bandwidth [BW = difference between the energy at $\mathbf{k} = (\pi, 0)$ and $(0, 0)$] and gap are BW $\approx 0.04 J_1, \Delta \approx 0.36 J_1$ [4], consistent with the measured values BW ≈ 0.3 meV and $\Delta \approx 3$ meV [8]. From the same analysis we estimate $J_2 \approx 61$ K ≈ 42 cm^{-1}. For the higher value of $J_2/J_1 = 0.678$ the bandwidth is approximately twice as large [4] which would make this ratio inconsistent with the neutron scattering data. Putting everything together we have the estimate for the singlet binding energy $\epsilon^S = Z^2 J_2 \approx 24$ cm^{-1}. Our experimental value for the lowest singlet mode in Fig. 1(b) with $E_2^S = 30$ cm^{-1} is $\epsilon_{\text{Raman}}^S \approx 18$ cm^{-1}.

The analysis based on the localized picture somewhat overestimates the binding since corrections of order $(J_2/J_1)^2$ and higher have been neglected. Such high-order corrections lead to the development of a strong dispersion as well as create several two-particle singlet modes with different energies, classified according to the group D_{2d}. Detailed calculations have recently been performed [16,17], providing quantitatively accurate results for the energies in the different symmetry sectors. Only the modes with $\Gamma_3(xy)$ symmetry contribute to the Raman intensity, and, as $T \to 0$, their contribution grows for the $(a'b')$ and vanishes for the (ab) geometry [17], consistent with our observations. In addition, the calculated energies [17] are in excellent agreement with the two lowest (30 and 46 cm^{-1}) singlet modes observed in our experiment, which we therefore interpret as two-particle bound states.

In $SrCu_2(BO_3)_2$ the four modes in Fig. 1(b) show ratios $E^S/\Delta = 1.25$–2.9. Two of the well-pronounced peaks (at 56 and 70 cm^{-1}) are above the two-particle threshold (2Δ). The smallness of the one-particle bandwidth makes it possible to resolve such higher energy peaks, since the weight of the scattering background is expected to be small. The pronounced sharpness of the peaks indicates that they can be interpreted as *three-particle excitations,* whose existence is indeed possible due to the localized nature of the states. A three-particle singlet bound state can be constructed as $|\Phi^S\rangle = \sum_{i,j,k} \phi_{i,j,k}^S (\mathbf{t}_i^\dagger \times \mathbf{t}_j^\dagger) \cdot \mathbf{t}_k^\dagger |0\rangle$, and its energy on the same level of approximation as discussed above (localized triplets) is $E_3^S = 3\Delta - Z^3 J_2 \approx 54$ cm^{-1}, in very good agreement with the energy of the mode at 56 cm^{-1}. The appearance of additional levels (as well as finite dispersion) at higher order is also expected. The total Raman scattering intensity, reflecting the presence of two- and three-particle singlets with spectral weights I_2 and I_3, is $I_B(\omega) = I_2 \delta(\omega - E_2^S) + I_3 \delta(\omega - E_3^S)$. In order to estimate the ratio of the two intensities we notice that while light couples directly to the singlet two-magnon state, the three-magnon state has to be created via the action of the Γ (magnon number nonconserving) term in Eq. (1) (i.e., this term provides a vertex correction to the Raman operator $R \sim \mathbf{t}_i^\dagger \cdot \mathbf{t}_j^\dagger$). Consequently, we estimate at $T = 0$, $I_3/I_2 \propto (J_2/J_1)^2 \approx 0.4$, in good agreement with the experimental ratio of 0.32 (at $T = 1.5$ K). Notice that in the hypothetical case $\Gamma = 0$, when the excitations are completely localized, the three-particle states do not contribute to the Raman intensity. Thus the Γ term plays an important role providing both a finite bandwidth and coupling to higher bound state modes. Let us also mention that three-particle bound states have been predicted theoretically in quasi-1D systems [11]. Our Letter presents the first experimental evidence for their existence in a (2D) dimerized spin system.

The bound state modes experience strong damping with increasing temperature [see Fig. 1(b)], due to scattering on thermally excited triplet states. The decrease of the scattering intensity I_B with temperature is governed by the density of excitations: $I_B(T) \propto (1 - Ae^{-\Delta/k_B T})$, where A is a constant. In Fig. 2(a) the integrated intensity of the bound states is shown together with a fit based on the equation above ($A = 215.7$) and fixing $\Delta = 34$ K from experimental data. The macroscopic temperature-induced population of triplet states has a direct effect on the excitation spectrum. For intermediate temperatures [5–100 K, typical spectrum shown at 7 K in Fig. 1(a)] a broad continuum of scattering is observed that is of magnetic origin [18]. However, in comparison with a 2D antiferromagnet with a maximum of the two-magnon continuum at $E_{\max} = 2.8$ J [19] its energy is very small. The reason for the maximum appearing at only 50 cm$^{-1} \approx 2\Delta$ is the smallness of the one-particle bandwidth in $SrCu_2(BO_3)_2$. The temperature dependence of the two-magnon scattering intensity shows a pronounced increase in the temperature range where the intensity of the bound states is dropping [see the open

triangles in Fig. 2(b)]. At higher temperatures (not shown here) it decreases again and is then superimposed on the intensity of quasielastic scattering. In Fig. 2(b) we compare the integrated scattering intensity with the behavior of the magnetic susceptibility $\chi(T)$. Calculations of the latter quantity exist, but their agreement with experiment is not fully satisfactory [1,4], and consequently we take $\chi(T)$ directly from experiment [1]. Notice that both the two-magnon continuum intensity and $\chi(T)$ exhibit strong variations on the same temperature scale, even though we are not aware of a rigorous sum rule relating the two quantities.

Quasielastic scattering connected with fluctuations of the magnetic energy density is found at high temperatures ($T > \Delta$) in our Raman scattering experiments. It has the expected Lorentzian spectral function [20]. To determine the evolution as a function of temperature we use the hydrodynamic form of the respective correlation function [21], which includes the magnetic specific heat $c_m(T)$ and the thermal diffusion constant D_T. In the high temperature approximation ($\hbar\omega/k_BT \ll 1$) the result is [20] $I(\omega) \propto \frac{k_B}{\hbar}\frac{c_m T^2 D_T k^2}{\omega^2+(D_T k^2)^2}$, where k is the scattering wave vector. A fit to this equation can then be used to estimate $c_m(T)$ from the integrated intensity, scaled by T^2. In Fig. 2(c) the result of this procedure is found in good agreement with the measured specific heat.

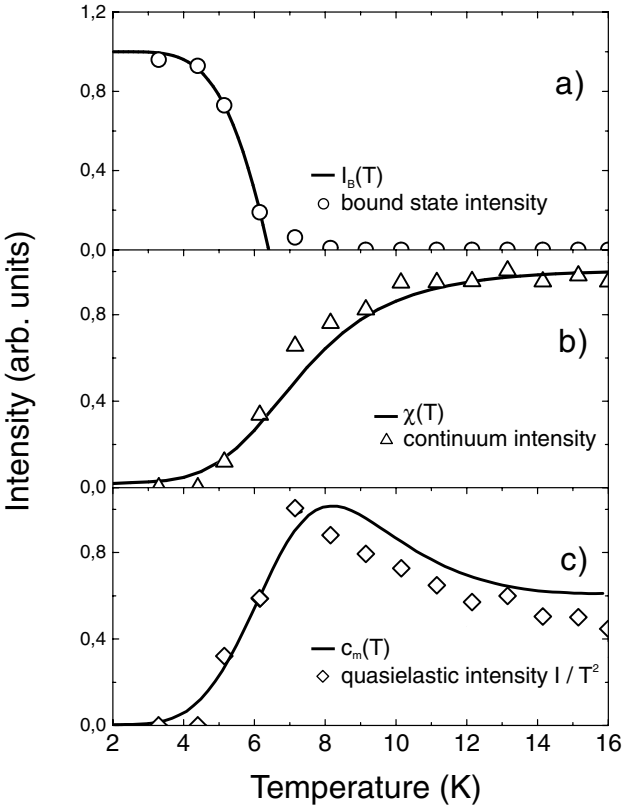

FIG. 2. Mapping of Raman scattering intensities (open symbols) on thermodynamic quantities (lines) as a function of temperature. The scattering intensities and the thermodynamic data from Refs. [1,6] are normalized to their maxima.

In conclusion, we have shown that the low-energy excitation spectrum of the 2D compound $SrCu_2(BO_3)_2$ has a rich and complex structure. Our main result is that at low temperature ($T \ll \Delta$) the spectrum contains several well-pronounced singlet modes which are interpreted as collective two-particle and novel three-particle singlet bound states of strongly localized triplets. We have demonstrated that since quantum fluctuations are absent in the ground state (due to the unique dimer arrangement), the triplet-triplet interactions can lead to large binding energies and scattering intensities, and consequently make the collective modes observable. At intermediate ($T \sim \Delta$) and high ($T \gg \Delta$) temperatures, where the quantum (interaction) effects are not important, the light scattering is dominated by a two-magnon continuum and quasielastic contributions. We relate the spectral weight evolution in these regimes to thermodynamic quantities.

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