Far-infrared study of the two-dimensional dimer spin system SrCu$_2$(BO$_3$)$_2$

T. Rööm, U. Nagel, E. Lippmaa
National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia

H. Kageyama, K. Onizuka, Y. Ueda
Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8666, Japan

Using far-infrared spectroscopy in magnetic fields up to 12 T we have studied a two-dimensional dimer spin gap system SrCu$_2$(BO$_3$)$_2$. We found several infrared active modes in the dimerized state (below 10 K) in the frequency range from 3 to 100 cm$^{-1}$. The measured splitting from the ground state to the excited triplet $M_S = 0$ sublevel is $\Delta_1 = 24.2$ cm$^{-1}$ and the other two triplet state sublevels in zero magnetic field are 1.4 cm$^{-1}$ below and above the $M_S = 0$ sublevel. Another multiplet is at $\Delta_2 = 37.6$ cm$^{-1}$ from the ground state. A strong electric dipole active transition polarized in the (ab)-plane is activated in the dimer spin system below 15 K at 52 cm$^{-1}$.

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1. INTRODUCTION

The discovery of high temperature superconductivity in lightly doped antiferromagnets has renewed interest in low dimensional spin systems with specific spatial structures. Recently a new two-dimensional spin gap system SrCu$_2$(BO$_3$)$_2$ was found. The SrCu$_2$(BO$_3$)$_2$ is interesting first, because the ground state is known. SrCu$_2$(BO$_3$)$_2$ has a tetragonal structure where structural dimers of Cu$^{2+}$ ions form an orthogonal network in the CuBO$_3$ planes, separated by Sr atoms. It is topologically equivalent to a system where the singlet dimer state is an exact eigenstate of the spin Hamiltonian. Second, for the first time among two-dimensional spin systems the quantized magnetization plateaus were observed. Third, SrCu$_2$(BO$_3$)$_2$ is close to the quantum critical transition point, $J' / J = 0.7$, from the gapful magnetic dimer state to the antiferromagnetically ordered gapless state. Fit of magnetic susceptibility data gives $J = 100$ K and $J' = 68$ K for the nearest neighbor and next-nearest neighbor antiferromagnetic coupling constants between copper $S = 1/2$ spins.

Despite the well-defined ground state, little is known about the excited states. The distance from the ground singlet state to the excited triplet state estimated from copper nuclear magnetic relaxation rate in a powdered sample is $\Delta_R = 30$ K. Submillimeter wave electron spin resonance (ESR) study on monocrystals shows that the excited triplet state splits into two triplet modes and the averaged value for the spin gap is 34.7 K. According to the same ESR study there must be another spin excitation above the triplet mode.

Infrared spectroscopy is a good method for studying excitations in a magnetic system because it is sensitive to spin, charge and lattice degrees of freedom. We present here the results of a low temperature (4 to 45 K) far-infrared study of SrCu$_2$(BO$_3$)$_2$ in magnetic fields from 0 to 12 T and at frequencies in the 3 to 100 cm$^{-1}$ range. We have determined the zero field splitting of the excited triplet state and have found a new strong infrared active resonance at 52 cm$^{-1}$.

![FIG. 1. Infrared absorption spectra of SrCu$_2$(BO$_3$)$_2$ for different light polarizations. (a) – absolute spectra in dimerized state (4.4 K) and in paramagnetic state (20 K). (b) – difference of 4.4 K and 20 K spectra. Spectrum in k||(ab), E$_1$∥c geometry has been lowered in vertical direction by 5 cm$^{-1}$.

We studied two single crystals of SrCu$_2$(BO$_3$)$_2$. The first sample was 0.17 mm thick in the c-direction and had an area of 10 mm$^2$ in (ab)-plane (CuBO$_3$ plane). This sample was used in the measurements where the light k vector was perpendicular to the (ab)-plane and electric field E$_1$ polarized in the (ab)-plane. The second sample consisted of two pieces 0.65 mm thick in a-direction and with a total area of 11.5 mm$^2$ in the (ac)-plane. This sample was used for measurements where the light k vector was in the (ab)-plane and E$_1$ either parallel to the c-axis or to the (ab)-plane.

Far-infrared measurements were done with a polarizing Martin-Pupplett Fourier transform spectrometer and a sample cryostat equipped with a 12 T Oxford In-
struments magnet and two $^3$He cooled silicon bolometers from Infrared Laboratories. Spectra were recorded at 0.4 cm$^{-1}$ resolution. The magnetic field was applied parallel to the direction of light propagation. Absolute absorption spectra $\alpha(\omega, T)$ were calculated from the transmission taking into account two back reflections from sample to vacuum interface: $\alpha(\omega, T) = -d^{-1} \ln[I(\omega, T)/I_0(\omega)(1-R)^2]$, where $I_0(\omega)$ is the intensity of the incident and $I(\omega, T)$ the intensity of the transmitted infrared radiation at frequency $\omega$; $d$ is the thickness of the crystal. The reflection coefficient $R = 0.33$ was calculated from the refraction index $n = 3.7$ determined from the fringe pattern of the 0.17 mm thick sample transmission spectrum.

Below 10 K several lines appear between 3 and 100 cm$^{-1}$ in the far-infrared transmission spectrum which is rather featureless for the paramagnetic (20 K) state (Fig. 1a). Strong features seen below 30 cm$^{-1}$ are due to light interference in the sample. Therefore, to see finer details we present in Fig. 1b spectra where the 20 K spectrum has been subtracted from the 4.4 K spectrum. The transmission does not change by more than few percents between 20 and 45 K. For $(\mathbf{k} \parallel (ab), \mathbf{E}_1 \parallel (ab))$ there are absorption lines at 24.2, 37.6, 43.0, 52, 69 and 84 cm$^{-1}$. The spectrum in $(\mathbf{k} \parallel c, \mathbf{E}_1 \parallel (ab))$ geometry is similar and is not plotted. When the electric field is perpendicular to the planes $(\mathbf{k} \parallel (ab), \mathbf{E}_1 \parallel c)$ only one line at 25.4 cm$^{-1}$ is present.

FIG. 2. Temperature dependence of absorption spectra in zero magnetic field. Inset (a) is a detailed view of the $T$ dependence of the singlet to triplet transition, $|S\rangle \rightarrow |T_0\rangle$. Side peaks at 22.7 and 25.4 cm$^{-1}$ are the $|S\rangle \rightarrow |T_{-1}\rangle$ and $|S\rangle \rightarrow |T_{+1}\rangle$ transitions.

Temperature dependence of the spectra is shown in Fig. 2 and 3. We have plotted the spectral weight (area under the line), full width at half maximum (FWHM) and peak positions of the 24.2 and 52 cm$^{-1}$ lines. For the 24.2 cm$^{-1}$ line a better fit was obtained with a Gaussian, while a Lorentzian was used for the 52 cm$^{-1}$ line. Analysis of the 52 cm$^{-1}$ line is complicated by a side peak at 53.5 cm$^{-1}$, and rapid broadening above 8 K. Therefore below 8 K we plot the spectral weight of the 52 cm$^{-1}$ line as a sum of spectral weights of two Lorentzians located at 52 and 53.3 cm$^{-1}$. Above 8 K we use a single Lorentzian fit.

Only the 24.2 and 37.6 cm$^{-1}$ lines split in a magnetic field (Fig.4). The 24.2 cm$^{-1}$ line corresponds to the transition from the ground singlet state $|S\rangle$ to the excited triplet state sublevel $|T_0\rangle$. This is obvious from the magnetic field dependence of the resonance frequency (Fig 4a). The line at 25.4 cm$^{-1}$ seen in Fig. 1b for $\mathbf{E}_1$ perpendicular to the planes is the $|S\rangle \rightarrow |T_{+1}\rangle$ transition because its resonance frequency increases with magnetic field (Fig. 4a, 4c). The third component of the triplet resonance, the $|S\rangle$ to $|T_{-1}\rangle$ transition, is seen when the magnetic field is applied, $\mathbf{B}_0 \parallel (ab)$, and
and consequently the Dzialoshinski-Moriya interaction \( |S\rangle \rightarrow |T_{+1}\rangle\), are too weak to be detected in Raman spectroscopy. The effect of the magnetic field on the singlet to triplet transition described so far is in changing the oscillator strength of the singlet to triplet transitions. Magnetic field, besides changing the oscillator strength, has another effect as shown in Fig. 5. Above 8 T lines start to broaden and to lose their intensity.

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E_1 \parallel (ab) \text{ (Fig 4c). There is an additional splitting of the triplet state field dependent components (open and filled triangles in Fig. 4a,4c) caused by anisotropic inter-dimer exchange interaction.} \]

Line positions of the triplet were fitted with \( E = \Delta \pm \sqrt{2E^2 + (g_{u}\beta B_0)^2} \), where \( \Delta = 24.15 \pm 0.05 \text{ cm}^{-1} \), \( E = 1.4 \pm 0.1 \text{ cm}^{-1} \) and in plane electron g-factor \( g_u = 2.06 \pm 0.06 \); Bohr magneton \( \beta = 0.469\text{ cm}^{-1}\text{T}^{-1} \). Within the error margins for both geometries \( E_1 \parallel c \) (Fig. 4a) and \( E_1 \parallel (ab) \) (Fig. 4c) the parameters are the same.

The resonance line at 37.6 cm\(^{-1}\) splits in the magnetic field into two components. From the magnetic field dependence of its resonance frequency we can identify these two transitions as transitions from the ground singlet state to the \( m_S = -1 \) and \( m_S = +1 \) sublevels of the \( S \geq 1 \) multiplet. The fit for this multiplet gives slightly different g-factors for the upper spin level, \( g_u = 2.08 \pm 0.04 \) and for the lower spin level, \( g_l = 2.02 \pm 0.01 \), with \( \Delta = 37.6 \text{ cm}^{-1} \) and \( E = 0 \).

From the magnetic field dependence of \( S = 1/2 \text{ Cu}^{2+} \) spin signal in the paramagnetic state at 20 K we determined the electron g-factor parallel to the planes, \( g_{1\parallel} = 2.04 \pm 0.04 \) and perpendicular to the planes, \( g_{1\perp} = 2.33 \pm 0.04 \). These are typical values for the \( \text{Cu}^{2+} \) spin in a tetragonal crystal field. If we normalize the paramagnetic \( \text{Cu}^{2+} \) signal to the temperature and energy splitting of the 24.2 cm\(^{-1}\) singlet-triplet transition in zero magnetic field at 4.4 K, we get that the spectral weight of the singlet to triplet transition is three times smaller than that of the paramagnetic signal. Magnetic dipole transitions between singlet (antisymmetric) and triplet (symmetric) states are forbidden. The antisymmetric Dzialoshinski-Moriya interaction mixes the singlet and triplet states and therefore makes the singlet-triplet transition possible. The local symmetry of a dimer is \( C_{2v} \) and consequently the Dzialoshinski-Moriya interaction \( J_{DM} \) does not vanish. The magnitude of \( J_{DM} \) is \( J_{DM} \approx (\Delta g/g)J_0 \) where \( \Delta g \) is the deviation of the electron g-factor from the free electron value, \( g \approx 2 \), and \( J_0 \) is the isotropic exchange interaction. If we use \( g_c = 2.28 \) (Ref. \[1\]) and \( J_0 = 24 \text{ cm}^{-1} \) we get \( J_{DM} = 2.9 \text{ cm}^{-1} \). The zero field splitting of the triplet resonance is \( 2E = 2.8 \text{ cm}^{-1} \), close to the estimate of \( J_{DM} \).

Variation of line intensities with magnetic field for the triplet state is observed. In \( k \parallel (ab), E_1 \parallel c \) (Fig. 4b) the \( |S\rangle \rightarrow |T_0\rangle \) resonance intensity increases from zero to 0.5 cm\(^{-1}\) with increasing magnetic field while the \( |S\rangle \rightarrow |T_{+1}\rangle \) loses its intensity. The \( |S\rangle \rightarrow |T_{-1}\rangle \) resonance intensity is below noise level. In \( k \parallel (ab), E_1 \parallel (ab) \) geometry (Fig. 4d) the 24.2 cm\(^{-1}\) line loses its intensity whereas transitions to \( |T_{-1}\rangle \) and \( |T_{+1}\rangle \) levels gain intensity. The intensity of the 37.6 cm\(^{-1}\) multiplet decreases nearly linearly with increasing field (not plotted). When the magnetic field is perpendicular to the planes the intensity of the \( |S\rangle \rightarrow |T_0\rangle \) transition (24.2 cm\(^{-1}\)) does not change with magnetic field. Other two components of the singlet to triplet transition, \( |S\rangle \rightarrow |T_{-1}\rangle \) and \( |S\rangle \rightarrow |T_{+1}\rangle \), are too weak to be detected in Raman spectroscopy. The effect of the magnetic field on the singlet to triplet transition described so far is in changing the oscillator strength of the singlet to triplet transitions. Magnetic field, besides changing the oscillator strength, has another effect as shown in Fig. 5. Above 8 T lines start to broaden and to lose their intensity.

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\text{FIG. 4. Magnetic field } B_0 \parallel k \text{ dependencies of line positions and spectral weights for two light polarizations at 4.4 K. Diamonds are the sums of spectral weights of the } |S\rangle \rightarrow |T_{-1}\rangle \text{ and } |S\rangle \rightarrow |T_{+1}\rangle \text{ transitions shown by open and filled triangles on (a) and (c) panels. Solid lines on panels (a) and (c) are the fits described in the text. Dashed line on panel (c) is the fit of Nojiri et al. of their ESR data.} \]

The 52 cm\(^{-1}\) resonance is active when the electric field is parallel to the (ab)-plane independent of the direction of light propagation (Fig. 1a). Because the light k-vector, \( E_1 \) and \( H_1 \) fields are orthogonal we come to the conclusion that the 52 cm\(^{-1}\) resonance is an electric dipole transition. This is also supported by the fact that the oscillator strength of the 52 cm\(^{-1}\) resonance is considerably larger than the oscillator strength of the high temperature paramagnetic \( \text{Cu}^{2+} \) signal or the 24 cm\(^{-1}\) singlet to triplet transition. We exclude the possibility of the 52 cm\(^{-1}\) resonance being a phonon. The first argument against being a phonon is the magnetic field effect. We found that above 8 T this line starts to lose its intensity. In the 12 T field the spectral weight is 1.4 times smaller than in zero field. The magnetic field effect on this resonance line is very similar to the effect of magnetic field on the singlet to triplet transition at 24 cm\(^{-1}\) (Fig. 5). The second argument is the temperature dependence. The 52 cm\(^{-1}\) transition starts to show up below 20 K (Fig. 3). To explain this kind of \( T \) dependence for a lattice mode one has to assume that a structural phase transition takes place and the Brillouin zone boundary
The magnetic field suppresses the singlet to triplet transition and the 52 cm\(^{-1}\) absorption line (Fig. 5). In SrCu\(_2\)(BO\(_3\))\(_2\), the first gapless ground state is reached at 21 T (Ref. 14). We observe that already the 9 T field is affecting line intensities. Other experiments have established similar low field effects. The magnetization starts to increase from its zero value in low fields and in ESR new multiple magnetic resonances have been detected above 12 T. Our experiment provides conclusive evidence that the magnetic fields smaller than the first critical field change the gapped ground state of the dimer system.

In conclusion, the spectrum of magnetic excitations in SrCu\(_2\)(BO\(_3\))\(_2\) in the dimerized state has several infrared active resonances. By their magnetic field dependence two of them have been identified as a triplet resonance at 24 cm\(^{-1}\) and as a multiplet at 37.6 cm\(^{-1}\). Third is a strong singlet resonance polarized in the (ab)-plane at 52 cm\(^{-1}\). Other three weak at 43, 69 and 84 cm\(^{-1}\) are singlet resonances.

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