Far-infrared study of the two-dimensional dimer spin system $SrCu_2(BO_3)_2$

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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}.

The discovery of high-temperature superconductivity in lightly doped antiferromagnets has renewed interest in low-dimensional spin systems with specific spatial structures. Recently a two-dimensional spin gap system $SrCu_2(BO_3)_2$ was found.[1] 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.[2] It is topologically equivalent to a system where the singlet dimer state is an exact eigenstate of the spin Hamiltonian.[3,4] *Second*, among two-dimensional spin systems the quantized magnetization plateaus were observed.[1] *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.[4–6] A 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. A submillimeter wave electron spin resonance (ESR) study[7] 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 (4–45 K) far-infrared study of $SrCu_2(BO_3)_2$ in magnetic fields from 0 to 12 T and at frequencies in the 3–100 cm^{-1} range. We have determined the zero-field splitting of the excited triplet state and have found a strong infrared-active resonance at 52 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 the (ab) plane ($CuBO_3$ plane). This sample was used in measurements where the light $\mathbf{k}$ vector was perpendicular to the (ab) plane and electric field $\mathbf{E}_1$ polarized in the (ab) plane. The second sample consisted of two pieces 0.65 mm thick in the 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 $\mathbf{k}$ vector was in the (ab) plane and $\mathbf{E}_1$ either parallel to the c axis or to the (ab) plane.

Far-infrared measurements were done with a polarizing Martin-Pupplett Fourier transform spectrometer[8] and a sample cryostat equipped with a 12 T Oxford Instruments 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 backreflections 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 ω; 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. 1(a)]. Strong features seen below 30 cm^{-1} are due to light interference in the sample. Therefore, to see finer details we present in Fig. 1(b) spectra where the 20 K spectrum has been subtracted from the 4.4 K spectrum. The transmission does not change by more than a few percent between 20 and 45 K. For $(\mathbf{k}\|(ab),\mathbf{E}_1\|(ab))$ there are absorption lines at 24.2, 37.6, 43.0, 52, 69, and 84 cm^{-1}. The spectrum in $(\mathbf{k}\|c,\mathbf{E}_1\|(ab))$ geometry is similar and is not plotted. When the electric field is perpendicular to the planes $(\mathbf{k}\|(ab),\mathbf{E}_1\|c)$ only one line at 25.4 cm^{-1} is present.

The temperature dependence of the spectra is shown in Figs. 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,

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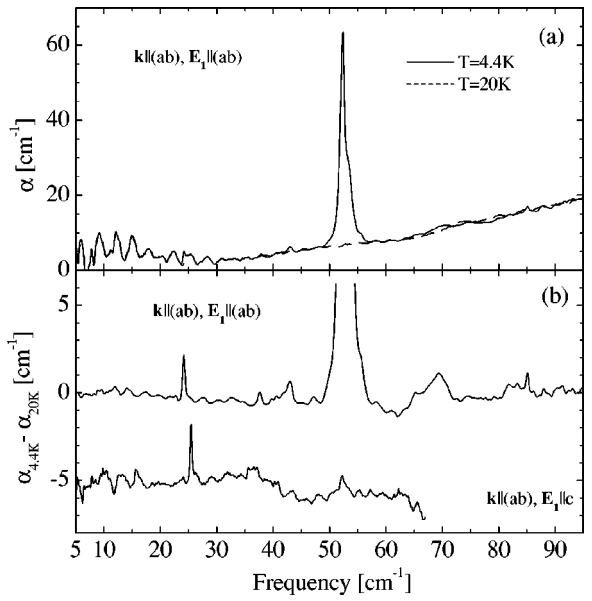

FIG. 1. Infrared absorption spectra of $SrCu_2(BO_3)_2$ for different light polarizations. (a) Absolute spectra in the dimerized state (4.4 K) and in the paramagnetic state (20 K). (b) Difference of 4.4 K and 20 K spectra. The spectrum in $\mathbf{k}\|(ab)$, $\mathbf{E}_1\|c$ geometry has been lowered in the vertical direction by 5 cm^{-1}.

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 [Figs. 4(a) and 4(c)].

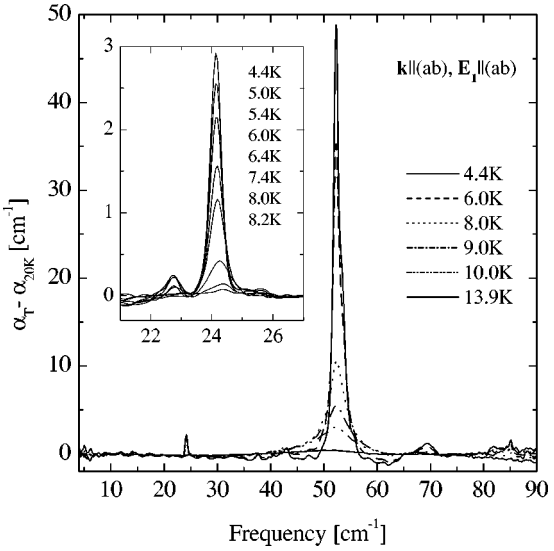

FIG. 2. Temperature dependence of absorption spectra in zero magnetic field. Inset (a) is a detailed view of the T dependence of the singlet to triplet transition $|S\rangle\rightarrow|T_0\rangle$. Side peaks at 22.7 and 25.4 cm^{-1} are the $|S\rangle\rightarrow|T_{-1}\rangle$ and $|S\rangle\rightarrow|T_{+1}\rangle$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

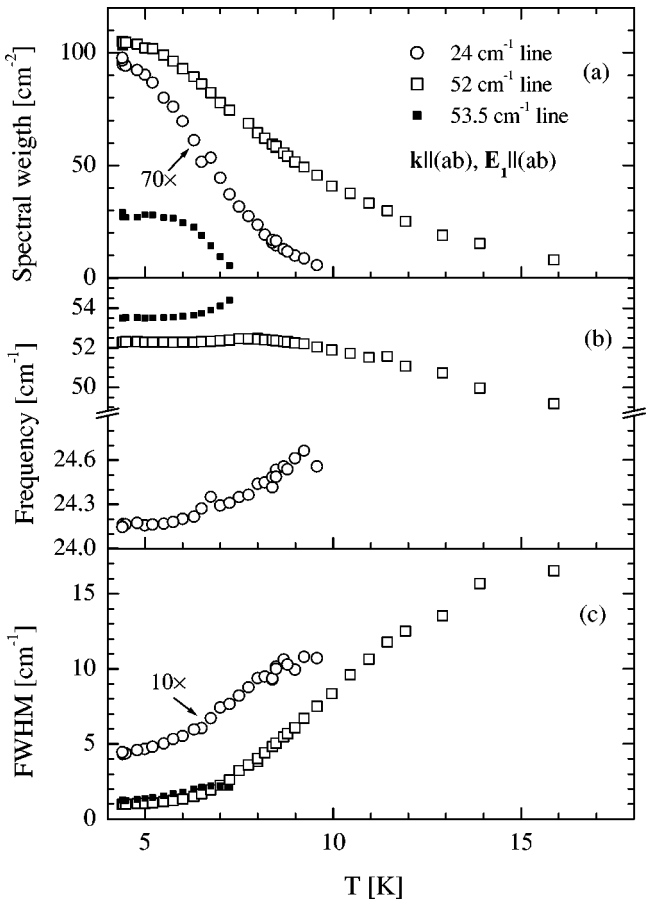

FIG. 3. Temperature dependencies of the 24, 52, and 53.5 cm^{-1} lines. (a) The spectral weight (area under the line). Below 8 K the spectral weight of the 52 cm^{-1} line is shown as the sum of two Lorentzian lines, one at 52 and the other at 53.5 cm^{-1}. (b) The line positions. (c) The full width at half maximum (FWHM).

The line at 25.4 cm^{-1} seen in Fig. 1(b) for $\mathbf{E}_1$ perpendicular to the planes is the $|S\rangle\rightarrow|T_{+1}\rangle$ transition because its resonace frequency increases with magnetic field [Figs. 4(a) and 4(c)]. The third component of the triplet resonance, the $|S\rangle$ to $|T_{-1}\rangle$ transition, is seen when the magnetic field is applied, $\mathbf{B}_0\|(ab)$ and $\mathbf{E}_1\|(ab)$ [Fig. 4(c)]. There is an additional splitting of the triplet-state field-dependent components [open and solid triangles in Figs. 4(a) and 4(c)] caused by anisotropic inter dimer exchange interaction.[7] Line positions of the triplet were fitted with $\mathcal{E}=\Delta\pm\sqrt{E^2+(g_i\beta B_0)^2}$, where $\Delta=24.15\pm0.05$ cm^{-1}, $E=1.4\pm0.1$ cm^{-1}, and, in plane electron g factor, $g_a=2.06\pm0.06$; the Bohr magneton $\beta=0.4669$ cm^{-1} T^{-1}. Within the error margins for both geometries $\mathbf{E}_1\|c$ [Fig. 4(a)] and $\mathbf{E}_1\|(ab)$ [Fig. 4(c)] 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 $S\geqslant1$ multiplet. The fit for this multiplet gives slightly different g factors for the upper spin level, $g_u=2.08\pm0.04$, and for the lower spin level, $g_l=2.02\pm0.01$, with $\Delta=37.6$ cm^{-1} and $E=0$.

From the magnetic field dependence of the $S=1/2$ Cu^{2+} spin signal in the paramagnetic state at 20 K we

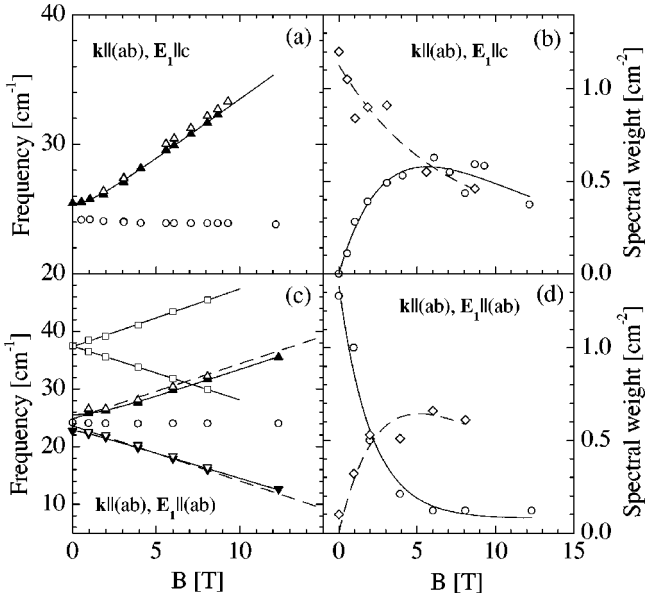

FIG. 4. Magnetic field $\mathbf{B}_0 \| k$ dependences of line positions and spectral weights for two light polarizations at 4.4 K. Diamonds are the sums of spectral weights of the $|S\rangle \rightarrow |T_{-1}\rangle$ and $|S\rangle \rightarrow |T_{+1}\rangle$ transitions shown by open and solid triangles in panels (a) and (c). Solid lines in panels (a) and (c) are the fits described in the text. The dashed line in panel (c) is the fit of Nojiri *et al.* of their ESR data (Ref. 7). Lines in panels (b) and (d) are drawn to guide the eye.

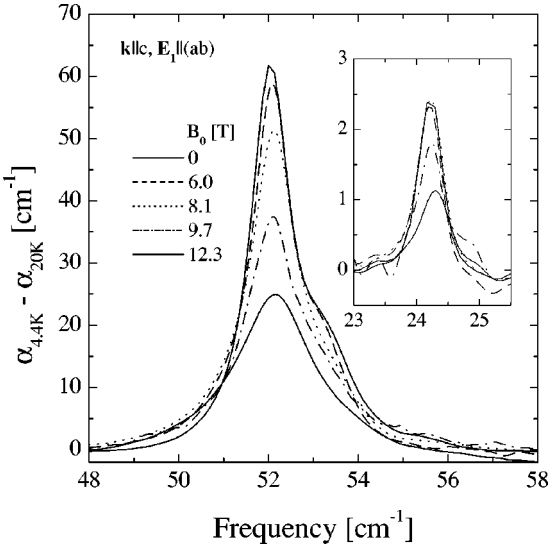

FIG. 5. Magnetic field effect on the 24 cm^{-1} (inset) and 52 cm^{-1} lines at 4.4 K.

determined the electron g factor parallel to the planes, $g_{\|} = 2.04 \pm 0.04$, and perpendicular to the planes, $g_{\perp} = 2.33 \pm 0.04$. These are typical values for the Cu^{2+} spin in a tetragonal crystal field.[9] If we normalize the paramagnetic 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 3 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[10] 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 Δg 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. 7) and $J_0 = 24$ cm^{-1}, we get $J_{DM} = 2.9$ cm^{-1}. The zero-field splitting of the triplet resonance is $2E = 2.8$ cm^{-1}, close to the estimate of J_{DM}.

Variation of line intensities with magnetic field for the triplet state is observed. In $\mathbf{k} \| (ab)$, $\mathbf{E}_1 \| c$ [Fig. 4(b)] the $|S\rangle \rightarrow |T_0\rangle$ resonance intensity increases from zero to 0.5 cm^{-2} 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 $\mathbf{k} \| (ab)$, $\mathbf{E}_1 \| (ab)$ geometry [Fig. 4(d)] 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. The 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 the far-infrared in this field orientation but were observed by ESR.[7] 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. The 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.

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. 1(b)]. Because the light $\mathbf{k}$, $\mathbf{E}_1$, and $\mathbf{H}_1$ 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 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 that the Brillouin zone boundary phonon is folded back to the zone center. However, there is no clear onset temperature of the 52 cm^{-1} resonance that could be identified as a structural phase transition temperature and also the width of the absorption line changes by more than one order of magnitude. This is not consistent with what is usually observed for a zone-folded phonon. Also, the Raman scattering experiment[11] has not shown any new phonon modes below 10 K and therefore there is no structural phase transition. We assign the 52 cm^{-1} line to a transition in the dimer spin system.

Creation of a single quasiparticle in the crystal by absorption of a light quantum is limited to long wavelengths of quasiparticles, $\mathbf{k} \approx 0$. An inelastic neutron scattering study[12] has found three branches of magnetic excitations in the dimerized state below 20 K. These excitations, in the **k** space points that are equivalent to the center of the Brillouin zone, are at 3, 5, and 9 meV. The 3 meV excitation corresponds to the singlet to triplet transition observed in infrared absorption at 24 cm^{-1} and also by ESR. In the infrared absorption there are two resonances at 37.6 and 43 cm^{-1} that are close in energy to the second branch at 5 meV. Two higher-energy absorption lines at 69 cm^{-1} and 84 cm^{-1} are close in energy to the third, 9 meV, branch. No magnetic excitations were detected in the inelastic neutron scattering experiment in the center of the Brillouin zone at 52 cm^{-1} (6.5 meV). We speculate that the 52 cm^{-1} absorption line in infrared corresponds to an electric dipole active transition where two triplet excitations are created simultaneously. In this type of transition the spin and the total momentum of two magnetic excitations is zero. For example, in antiferromagnets it has been shown that the second-order electric dipole transition is stronger than the first-order magnetic dipole transition.[13]

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 (Refs. 1 and 14). We observe that already the 9 T field is affecting the line intensities. Other experiments have established similar low-field effects. The magnetization starts to increase from its zero value in low fields[1,14] and in ESR (Ref. 7) multiple magnetic resonances have been detected above 12 T. Our experiment provides conclusive evidence that 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}. The third is a strong singlet resonance polarized in the (ab) plane at 52 cm^{-1}. The other three weak resonances at 43, 69, and 84 cm^{-1} are singlet resonances.

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