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Magnetic excitations and optical transitions in the multiferroic spin-$\frac{1}{2}$ system $LiCu_2O_2$

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Magnetic excitations in a cycloidal magnet $LiCu_2O_2$ are explored using terahertz absorption spectroscopy in magnetic fields up to 12 T. Below the spin ordering temperature, eight optically active transitions are observed in the spin system of $LiCu_2O_2$ in the range from 4 to 30 cm^{-1}. In magnetic field the number of modes increases and the electric polarization flop is seen as a change in magnetic field dependence of mode energies. The polarization dependence of two of the modes in zero magnetic field fits the selection rules for the cycloid tilted by $\theta=(41\pm1)°$ from the *bc* plane. For the remaining six modes electric and magnetic dipole approximations cannot explain the observed polarization dependence. The electromagnon is not seen in the explored energy range although there is evidence that it could exist below 4 cm^{-1}.

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The coupling between magnetic and electric orders in multiferroic materials makes them attractive for technological applications. An especially interesting class of multiferroics is frustrated magnets, where the charge order is driven by the magnetic order[1] and even moderate magnetic fields are sufficient to select between different magnetic ground states and change the charge order due to magnetoelectric (ME) coupling. The ME interaction transfers part of the electric dipole moment of the charge-ordered state to the spin waves enhancing their ability to absorb electromagnetic waves, typically in the terahertz range.[2,3] *A priori*, the knowledge of the strength of the static ME coupling for a given material does not tell us the strength of the dynamic ME coupling. Therefore, the exploration of terahertz properties is of interest to fully exploit multiferroic materials.

The spin cycloid is an example of a frustrated magnetic structure where ME coupling is allowed. In the spin cycloid the electric polarization is induced either through the spin current[4] or the inverse Dzyaloshinskii-Moriya (DM) interaction mechanism.[5,6] In a one-dimensional chain of spins along the *y* axis with spins rotating in the *yz* plane, the electric polarization $\mathbf{P}=(0,0,P)$ is perpendicular to the cycloidal ordering vector $\mathbf{Q}=(0,Q,0)$ and perpendicular to the normal of the spin rotation plane, $\mathbf{P}\propto\mathbf{Q}\times(\mathbf{S}_i\times\mathbf{S}_{i+1})$ [see Fig. 1(b)]. The orientation of the spin rotation plane is determined by anisotropic interactions, such as easy-plane anisotropy or DM interaction. Several multiferroic materials have a cycloidal spin order: $TbMnO_3$, $DyMnO_3$,[7–9] $Ni_3V_2O_8$,[10] $LiCu_2O_2$,[11] $LiVCuO_4$,[12] and CuO.[13] Although $LiCu_2O_2$ seems to be a good model system with prevailing one dimensionality of its magnetism, the connection between the electric polarization and the underlying magnetic structure is not well understood.

The structure of $LiCu_2O_2$, shown in Fig. 1(a), contains Cu-O chains extending along the crystallographic *b* axis. The chains form a zigzag Cu^{2+} $S=1/2$ spin ladder with the ladder plane tilted out from the *bc* plane.[14] The ladders in the planes, stacked along the *c* axis, have an alternating tilt angle of $\pm38.4°$ leading to two inequivalent ladders per unit cell. The first magnetic phase transition is at 24.6 K into the sinusoidal spin structure.[15] An incommensurate cycloidal spin order with $\mathbf{Q}\|\mathbf{b}$, driven by frustrated isotropic exchange interactions inside the ladders, appears in the second phase transition[15–17] below 23 K together with spontaneous polarization[11] $\mathbf{P}\|\mathbf{c}$. The knowledge about the orientation of the cycloid plane is controversial. Initially an *ab* plane cycloid was considered in the neutron scattering study.[16,18] How-

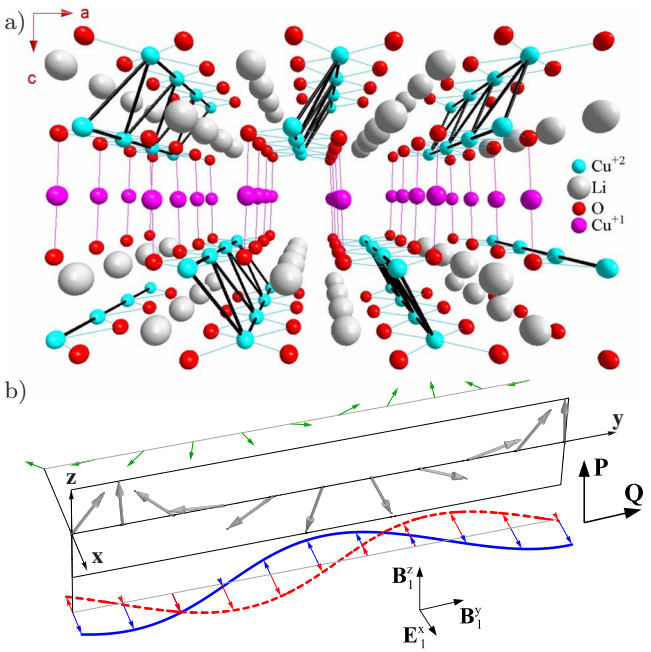

FIG. 1. (Color online) (a) Crystal structure of $LiCu_2O_2$. Cu^{2+} spins, joined by thick black lines, form a zigzag spin ladder. (b) Cycloidal order of spins $\mathbf{S}_i$ positioned along the *y* axis, shown with thick arrows. Thin arrows show the change $\delta\mathbf{S}_i$ to visualize the spin-wave dynamics. The ω_y and ω_z modes change $\mathbf{S}_i$ in *x* direction and are drawn by blue (gray) arrows in solid line envelope and red (light gray) arrows in dashed line envelope, respectively. Green arrows in the *yz* plane show the ω_x mode.

ever, the direction of **P** together with the inverse DM mechanism dictates a *bc* plane cycloid.[11] A later study by Seki *et al.*[19] confirmed the *bc* plane cycloid and $\mathbf{P}\|\mathbf{c}$. However, they found deviations from the *bc* cycloid in accord with the NMR study.[17] The presence of ME coupling in $LiCu_2O_2$ is demonstrated by the flop of polarization from $\mathbf{P}\|\mathbf{c}$ to $\mathbf{P}\|\mathbf{a}$ if magnetic field $\mathbf{B}_0 > 2$ T is applied along the *b* axis.[11] Such a flop can be explained by invoking a ME coupling between two spin chains in neighboring ladder planes.[20] Also, resonant soft x-ray magnetic scattering shows evidence that the interchain spin coupling along the *c* direction is essential for inducing polarization.[21]

Modes at wave vectors $\mathbf{k}=0$ and $\mathbf{k}=\pm\mathbf{Q}$ couple to long-wavelength electromagnetic radiation within the linear spin-wave model of a spin cycloid. They correspond, as shown in Fig. 1(b), to the rotations of spins about three axes by small angles.[2] The rotation about the *x* axis ($\mathbf{k}=0$) costs no energy because the spins rotate within the easy plane; hence, $\omega_x=0$. Rotations about two other axes have finite energies, $\omega_y=\omega_z$, with the magnitude determined by the size of the easy-plane anisotropy. The motion of spins induced by magnetic component $\mathbf{B}_1$ of terahertz radiation is described by $\delta\mathbf{S}_i/\delta t \propto \mathbf{B}_1 \times \mathbf{S}_i$. Accordingly, all three modes are magnetic dipole active, $\mathbf{B}_1^y$ excites ω_y and $\mathbf{B}_1^z$ excites ω_z with equal intensity in zero field; $\mathbf{B}_1^x$ excites ω_x although this mode has zero energy. In the presence of dynamic ME coupling, the ω_y mode is excited by the electric component $\mathbf{E}_1^x$ of terahertz radiation[2] and is referred to as the electromagnon.[22] Thus, the orientation of the spin cycloid can be determined from the polarization dependence of terahertz absorption.

In this Rapid Communication we study the magnetic field and the polarization dependence of the terahertz absorption in the cycloidal phase of $LiCu_2O_2$. Our aim is to find the electromagnon, the orientation of the spin cycloid, and changes in the spin excitation spectrum upon the polarization flop in 2 T field. Previously, a terahertz absorption study on $LiCu_2O_2$ has been reported[23] where a peak at 12 cm^{-1} with increasing energy in the field $\mathbf{B}_0\|\mathbf{c}$ was found.

Three single-crystal samples were measured from the same batch as in Ref. 11. Sample L1 had an *ab* plane area of 6.16 mm^2 and a thickness of 0.75 mm in the *c* direction and samples L2 and L3 had *ac* plane areas of 1.44 and 6.88 mm^2 with thicknesses of 1.75 and 4.3 mm in the *b* direction, respectively. Since the crystals were twinned in the *ab* plane, with a twin size on the order of 10 μm, we use *a*(*b*) notation when referring to direction-sensitive physical properties. Terahertz absorption spectra were recorded using a Martin-Puplett spectrometer with a 0.3 K bolometer and a rotatable polarizer in front of the sample.[24]

Several strong phonon absorption lines are seen in the absolute spectra in Fig. 2. The differential spectrum in Fig. 2(b) shows that only the lines below 35 cm^{-1} that disappear above the cycloidal ordering temperature $T=23$ K are spin-wave excitations. In the rest of this Rapid Communication we use the 0 T spectrum at 30 K as a reference spectrum by subtracting it from the spectra measured in the given field and at lower *T*.

Two peaks are emerging already in the 24 K spectrum in the sinusoidal phase and are easily seen at 23 K [Fig. 2(c)]. As *T* drops the peak energies increase and eventually at least

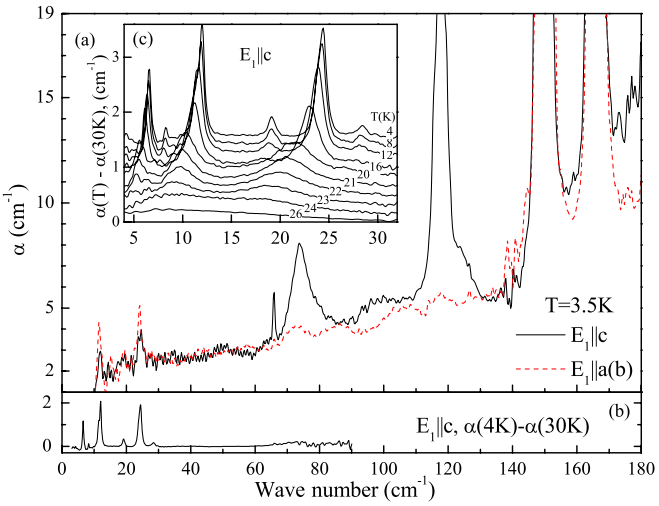

FIG. 2. (Color online) Light absorption in $LiCu_2O_2$ (sample L3) below 180 cm^{-1} measured in $\mathbf{E}_1\|\mathbf{a}(\mathbf{b})$ (dashed red line) and $\mathbf{E}_1\|\mathbf{c}$ (solid black line) polarizations. *T* dependence of absorption, $\mathbf{E}_1\|\mathbf{c}$, is shown by differential absorption spectra in (b) and in the inset (c).

six peaks can be seen in the 4 K spectrum. Higher-resolution spectra show that the two strongest peaks at 12 and 24 cm^{-1} are doublets, split by 0.8 cm^{-1} (Fig. 3). This increases the total number of peaks to eight (Table I). As $\mathbf{B}_0$ is applied (Fig. 4) lines shift, change their intensity, and some split. In fields stronger than 5 T, new modes, G and H, emerge into the spectral window from the low-energy side [Fig. 4(c)]. The expected number of optically active modes within the spin-wave approximation is two: ω_y and ω_z. There are two spin chains in the unit cell and the coupling between the chains in the *c* direction may split C and E modes into C^1, C^2 and E^1, E^2. In addition, if the cycloid is not circular, ellipticity activates otherwise optically silent modes at multiples of the ordering vector $\pm nQ$.[25] However, the electric dipole ac-

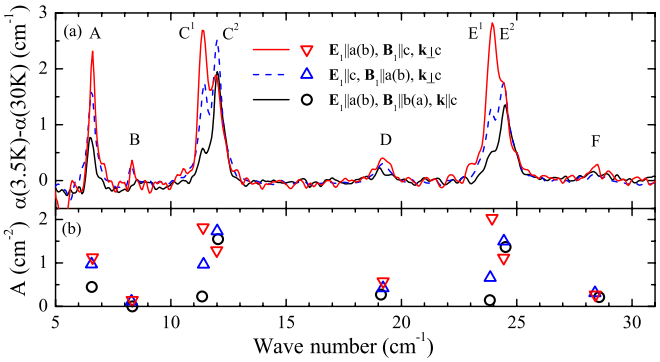

FIG. 3. (Color online) Polarization dependence of absorption in $LiCu_2O_2$ below 35 cm^{-1}, $T=3.5$ K, and $B_0=0$ T. (a) Differential absorption spectra are shown by curves and (b) absorption line areas from Lorentzian fits are given by symbols for following polarizations: black solid line and circles for $\mathbf{E}_1\|\mathbf{a}(\mathbf{b}), \mathbf{B}_1\|\mathbf{b}(\mathbf{a})$ are an average of spectra measured on samples L1 and L2; red (gray) solid line and down triangles are for $\mathbf{E}_1\|\mathbf{a}(\mathbf{b}), \mathbf{B}_1\|\mathbf{c}$, sample L2; blue dashed line and up triangles are for $\mathbf{E}_1\|\mathbf{c}, \mathbf{B}_1\|\mathbf{a}(\mathbf{b})$, sample L2. The letters from A to F in (a) label lines (see Table I).

TABLE I. Spin excitations observed in the terahertz absorption spectra of $LiCu_2O_2$ at $T=3.5$ K and $B_0=0$ T. Best fit Lorentzian parameters: line position $\tilde{\omega}_0$ (cm^{-1}), linewidth at half maximum γ (cm^{-1}), and line area A (cm^{-2}) are listed for three different orientations of $\mathbf{E}_1$ and $\mathbf{B}_1$.

	$\mathbf{E}_1 \| a(b), \mathbf{B}_1 \| b(a)$			$\mathbf{E}_1 \| \mathbf{c}, \mathbf{B}_1 \| a(b)$			$\mathbf{E}_1 \| a(b), \mathbf{B}_1 \| \mathbf{c}$		
	$\tilde{\omega}_0$	γ	A	$\tilde{\omega}_0$	γ	A	$\tilde{\omega}_0$	γ	A
A	6.6	0.3	0.5	6.6	0.4	1.0	6.6	0.3	1.1
B				8.3	0.2	0.1	8.3	0.2	0.1
C^1	11.4	0.3	0.2	11.4	0.4	1.0	11.4	0.4	1.8
C^2	12.1	0.5	1.5	12.0	0.5	1.7	12.0	0.5	1.3
D	19.1	0.8	0.3	19.2	0.7	0.4	19.2	0.8	0.6
E^1	23.8	0.3	0.1	23.9	0.5	0.7	23.9	0.5	2.0
E^2	24.5	0.7	1.4	24.5	0.6	1.5	24.4	0.6	1.1
F	28.6	1.2	0.2	28.4	1.2	0.3	28.4	0.7	0.6

tive isotropic exchange modulation mechanism that couples light to the spin wave at the Brillouin-zone boundary[3] is not active because optically active spin modes in $LiCu_2O_2$ are below 30 cm^{-1} while the zone-boundary energy of the spin waves in the b direction is 7 meV (56 cm^{-1}).[18]

The polarization dependence of terahertz absorption spectra is presented in Fig. 3 and fit results of the absorption lines are given in Table I. Our measurement rules out both *ab* and *bc* plane spin cycloids within the selection rules discussed above and outlined in Fig. 1(b). For the $LiCu_2O_2$ crystal structure a model where there are two cycloids corresponding to two zigzag chains, tilted out from the *bc* plane by an angle $\pm\theta$, seems natural. The absorption line area for the $\mathbf{B}_1 \| \mathbf{c}$ polarization becomes $A_c = 4A_0 \cos^2\theta$ with A_0 standing for the line area when $\mathbf{B}_1$ is in the cycloid plane. The factor 4 accounts for two cycloids per unit cell times two twin domains. For $\mathbf{B}_1$ in the *ab* plane, the line area is $A_{ab} = 2A_0(\sin^2\theta + 1)$, where the first term in parentheses is from $\mathbf{B}_1 \perp \mathbf{b}$ domains and the second one is from $\mathbf{B}_1 \| \mathbf{b}$ domains. Lines C^2 and E^2 satisfy this model and give $\theta = (41 \pm 1)°$ for the cycloid tilt angle, which is close to the crystallographic tilt angle of 38.4° of the zigzag chains. But the tilted cycloid model does not explain the polarization dependence of other lines. Moreover, the magnetic and the electric dipole approximations do not hold for lines A, C^1, and E^1. They are weakest when light propagates parallel to the c axis and stronger when light propagates perpendicular to the c axis. In the dipole approximation the absorption line area depends on the orientation of light polarization with respect to the crystal axes and not on the orientation of the **k** vector of light. Possible explanations to the observed **k** dependence can be the circular dichroism or electric quadrupolar transitions, but further theoretical study is required.

Two cases of magnetic resonance in helical structures have been treated theoretically in the spin-wave approximation: $\mathbf{B}_0$ perpendicular to the spin rotation plane and $\mathbf{B}_0$ in the plane of spin rotation.[26–29] These results cannot be directly adapted to our experiment since the magnetic field would be perpendicular to the cycloidal plane only for an *ab* or a *bc* plane circular cycloid in $LiCu_2O_2$. Given the complexity and the quantum nature of the problem, the theoretical description of spin-wave modes in $LiCu_2O_2$ is not within the scope

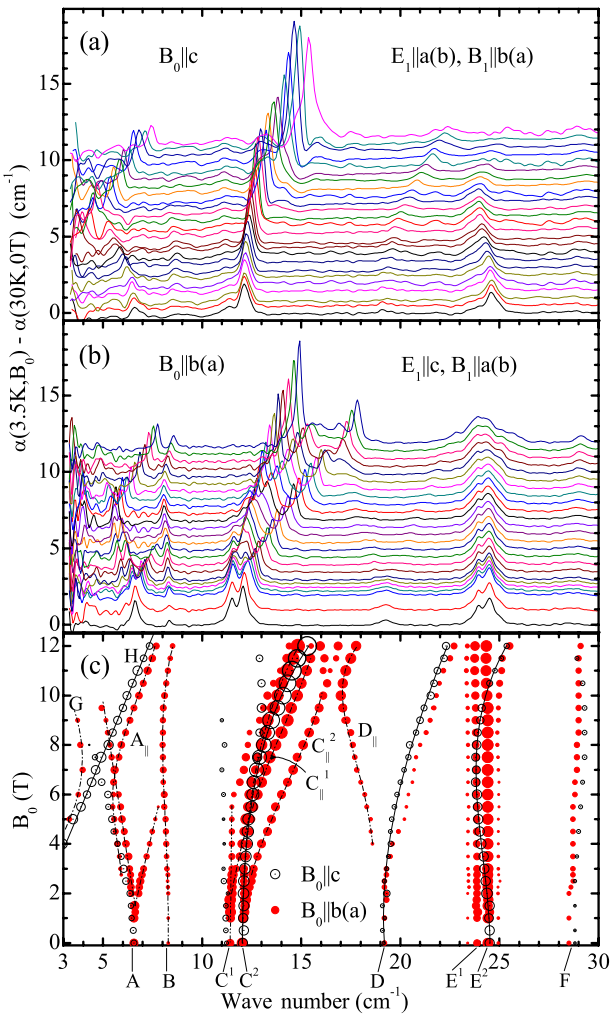

FIG. 4. (Color online) $\mathbf{B}_0$ dependence of terahertz absorption in $LiCu_2O_2$ at 3.5 K. Differential absorption spectra (a) $\mathbf{B}_0 \| \mathbf{c}$ and $\mathbf{E}_1 \| \mathbf{a}(\mathbf{b}), \mathbf{B}_1 \| \mathbf{b}(\mathbf{a})$, sample L1 ; (b) $\mathbf{B}_0 \| \mathbf{b}(\mathbf{a}), \mathbf{E}_1 \| \mathbf{c}, \mathbf{B}_1 \| \mathbf{a}(\mathbf{b})$, sample L2. (c) has the results of Lorentzian fits where the area of the symbol is proportional to the absorption line area A; black empty circles $\mathbf{B}_0 \| \mathbf{c}$ and filled red (gray) circles $\mathbf{B}_0 \| \mathbf{b}(\mathbf{a})$. Black solid and dashed-dotted lines are eye guides, except line H which is a linear fit of line position as a function of B_0.

of the current Rapid Communication. The number of modes is larger in Fig. 4(b) than in Fig. 4(a) because two crystal domains, $\mathbf{B}_0\|\mathbf{b}$ and $\mathbf{B}_0\perp\mathbf{b}$, contribute to the absorption; in $\mathbf{B}_0\|\mathbf{c}$ twin domains are equal with respect to the field. Some changes are evident in the terahertz absorption spectra around 2 T [Fig. 4(b)]. This is due to reordering of spins when **P** flops from *c* to *a* axis. Line A splits between 1 and 2 T and lines C^1 and C^2 acquire dispersing modes $C^1_\|$ and $C^2_\|$ [Fig. 4(c)]. We assign the $C^1_\|$ and the $C^2_\|$ modes together with new modes $A_\|$ and $D_\|$ to domains where $\mathbf{B}_0\|\mathbf{b}$ since this is the field direction where **P** is flopped. There is some evidence [Fig. 4(c)] that $\mathbf{A}_\|$ and G modes anticross and therefore the G mode may belong to the $\mathbf{B}_0\|\mathbf{b}$ domains.

Electromagnons contribute to the static dielectric constant as $\Delta\varepsilon=\varepsilon(0)-\varepsilon_\infty=\Sigma_j(\omega_p^j/\tilde{\omega}_0^j)^2$, where the sum runs over all spin-wave modes observed below 35 cm^{-1} in the $\mathbf{E}_1\|\mathbf{a}$ terahertz absorption spectrum; $\tilde{\omega}_0^j$ and ω_p^j are the *j*th mode resonance energy and plasma frequency, both in wave number units (ω_p^j is related to line area by $\pi\omega_p^j=\sqrt{An}$ with refraction index $n=3.36$ for $\mathbf{E}_1\|\mathbf{a}$); and ε_∞ contains the contribution from all other modes above 35 cm^{-1} and is taken *T* independent below 30 K.[30] Assuming that all the oscillator strength is due to electric dipole activity, we can set an upper limit to $\Delta\varepsilon_a=0.024$ using $\mathbf{E}_1\|\mathbf{a}(\mathbf{b}),\mathbf{B}_1\|\mathbf{c}$ data from Table I. A measurement at 28 kHz gave $\Delta\varepsilon_a=0.1$,[11] which is four times larger. However, the B_0 dependence shows [Fig. 4(c)] that there is an additional mode (H) which shifts into our measurement window at linear rate of 0.522 ± 0.005 cm^{-1} T^{-1} with a zero-field intercept at 1.03 ± 0.05 cm^{-1}. Assuming the same oscillator strength for the zero-field resonance as is above 5 T, we get that the contribution of mode H to the dielectric constant is $\Delta\varepsilon_a=0.46$. The actual number might be smaller because it is not known if, first, $\omega_p=$const, and second, whether $\tilde{\omega}_0\propto B_0$ persists down to zero field. A mode at 1 cm^{-1}, when extrapolated to 0 T, has been detected with an electron-spin-resonance technique although with nonlinear B_0 dependence.[31]

In conclusion, the analysis of the terahertz absorption spectra within the linear spin-wave theory shows that the spin order is not *ab* nor *bc* plane cycloid. The cycloid tilt angle of $(41\pm1)^\circ$ out of the *bc* plane is inferred from the polarization dependence of two modes assuming that they are magnetic dipole active. For other modes the polarization dependence is not compatible with magnetic or electric dipole activity of a cycloidal spin chain. We have evidence that a spin-wave mode at 1 cm^{-1} has sufficient oscillator strength to be an electromagnon. Understanding the origin of the large number of optically active spin excitations and their interaction with magnetic field in a quantum spin system such as $LiCu_2O_2$ requires further theoretical investigation.

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