

Infrared spectroscopy of tetrahedral quantum spin systems $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ ($\text{X}=\text{Br}$ and Cl)

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Abstract. $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$, with $\text{X}=\text{Br}$ and Cl , are spin-tetrahedral systems displaying magnetic ordering at low temperatures. We have performed optical reflectivity measurements over a broad spectral range as a function of temperature and magnetic field. We have identified the resonance frequencies of the infrared optically active phonon modes and estimated the value of the electronic gap in both tellurate compounds. No variation of the spectra has been observed while crossing the magnetic ordering transition temperature or by applying a magnetic field. The implications of these findings are discussed in relation to the nature of the phase transition.

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1 Introduction

Low dimensional quantum spin systems are of great interest due to the number of exotic properties they exhibit and to the analogies they present with high temperature superconductors [1]. The reduced dimensionality, in combination with frustration, increases quantum fluctuations and the conventional picture of a long-range ordered Néel ground state breaks down. The resulting spin liquid ground state is characterized by finite zero temperature correlation length and by the opening of a spin gap [2,3]. In this respect, the $S = 1/2$ pyrochlore lattice deserves special attention, since it is believed to have very short correlation length and a spin-triplet gap, eventually filled with low-lying singlet states [4]. It has been shown [4] that a one-dimensional (1D) array of coupled tetrahedra can be seen as a 1D analog of the pyrochlore lattice.

The recently discovered tellurates $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ with $\text{X}=\text{Br}$ and Cl offer the opportunity to investigate the interplay of frustration and reduced dimensionality in a $S = 1/2$ tetrahedral quantum spin system. Their structure is made of Cu^{2+} (coupled) tetrahedra aligned in tubes along the c -axis direction (Fig. 1). The substitution of Br with Cl causes a decrease of the unit cell volume by 7% which is expected to increase the value of the inter-tetrahedral coupling constant J_c . Even if the susceptibility can be fitted – at least in a first approximation – with a

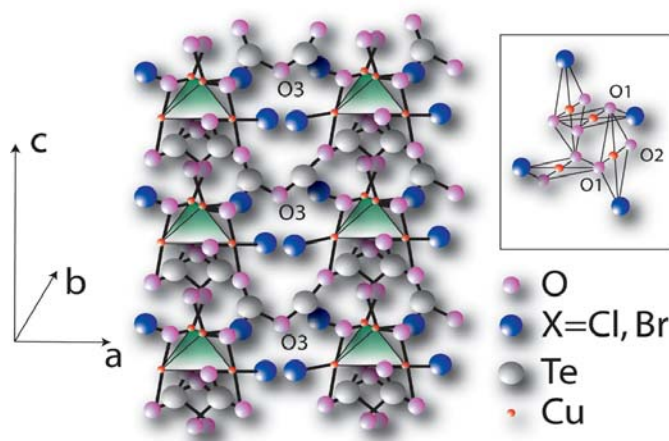


Fig. 1. Schematic crystal structure of $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$, with $\text{X}=\text{Br}$ and Cl , emphasizing the line-up of the Cu^{2+} tetrahedra. The structure contains three inequivalent oxygen positions. The O atoms between the chains of the Cu^{2+} tetrahedra are denoted by O3. The inset shows the Cu_4 tetrahedron with the O1-O1-O2-X idealized squares and the Cu^{2+} ion in the center [5].

model of non-interacting tetrahedra, J_c plays a key role in determining the ground state properties of the two compounds. Both systems undergo a magnetic ordering phase

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transition at $T_0 = 18.2$ K and 11.4 K for the Cl and Br compound, respectively [6]. The ordering in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ seems to be of 3D antiferromagnetic type [7] while in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ it is more unconventional and reminiscent of a spin liquid ground state [6].

Magnetic light scattering on $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$, with incoming and outgoing electric fields polarized along the c direction, displays the presence at high temperatures of a pyramidal-shaped scattering continuum at about 60 cm^{-1} , attributed to a two-magnon-like scattering process [6,8], and of a longitudinal magnon mode at 16 cm^{-1} for reduced temperatures [9,10]. It has been proposed [6,11] that a dimerized phase due to the distortion of the tetrahedra might be at the origin of the ordering transition at 11.4 K in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$, leading to a spin Peierls (SP)-like scenario. Experimental evidence for such a distortion was, however, never established. A structural transformation mediated by strong spin-lattice coupling was also put forward for the transition of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ (Ref. [12]). This would imply orbital ordering via the Jahn-Teller mechanism.

Infrared (IR) spectroscopy is a powerful technique to investigate structural phase transitions. The folding of the Brillouin zone after a SP transition leads to superlattice reflections and may activate several phonon modes. Moreover, the lattice instability could lead to the softening of the phononic branch involved in the distortion (the so-called soft mode), and the red shift of an optical phonon may be probed at the Γ point by optical techniques. Magnetic excitations are in principle not accessible to IR light because of the vanishing of the electric dipole moment. However, it has been shown [13,14] in 2D cuprates, that phonon-assisted magnetic excitation processes are optically allowed due to a lowering of the lattice symmetry. Furthermore, optically active magnetic excitations were found in the $\alpha\text{-NaV}_2\text{O}_5$ ladder compound [15], and the $k = 0$ spin-gap of CuGeO_3 has been observed by IR transmission measurements [16]. Our study was therefore motivated by the possibility of finding optical signatures of the magnetic ordering phase transition in the $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ and $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ compounds.

2 Experiment and results

High purity samples were prepared from mixtures of lone electron pair cations such as Se(IV), Te(IV) and Bi(III) with chlorine or bromine ions [17,18]. Typical dimensions were about 4 mm along the c -axis and 2 mm in the transverse direction. Our specimens are from the same production as those employed in references [6,12]. An ample characterization with ac susceptibility measurements has been performed, giving identical and fully reproducible results which confirm the transition to a magnetic ordering phase below T_0 (see, e.g., Fig. 2 in Ref. [6] and Figs. 1 and 2 in Ref. [12]).

We have measured the optical reflectivity $R(\omega)$ of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ and $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ from the far IR up to the ultraviolet as a function of temperature (10–300 K) and magnetic field H (0–7 T) oriented perpendicularly to

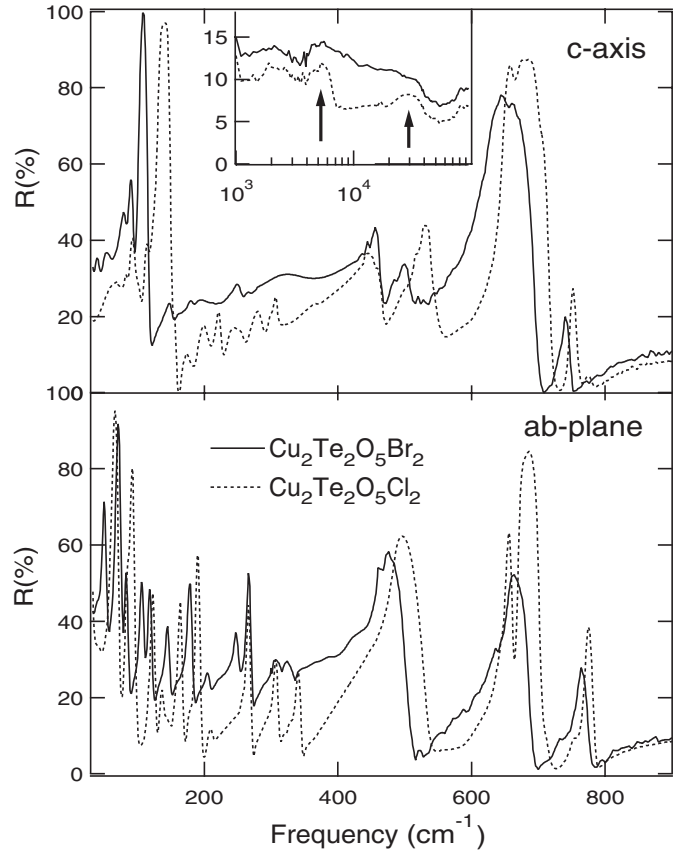


Fig. 2. Optical reflectivity of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ and $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ single crystals with light polarized along the c -axis (upper panel) and within the ab -plane (lower panel). The inset in upper panel shows the high energy part ($\omega > 1000\text{ cm}^{-1}$) of the spectra with $E \parallel c$; the reflectivity curves at high energies within the ab -plane (not shown here) display the same features observed along the chain direction.

the c -axis (Fig. 1). In order to probe the anisotropy of the excitations, light was polarized along the chain direction (c -axis) and along the transverse direction lying within the ab -plane. The data acquisition has been performed with a Bruker Fourier spectrometer equipped with an Oxford magnet cryostat with appropriate optical windows. Kramers-Kronig (KK) transformations were used to calculate the real part $\sigma_1(\omega)$ of the optical conductivity [19].

We present in Figure 2 the optical reflectivity spectra of the two compounds at $T = 20$ K, and for both polarization directions. The curves are reliable down to 30 cm^{-1} , and are not affected by Fabry-Perot interferences which were sometimes encountered in the low energy spectra of the insulators [20]. Strong optical phonon modes characterize the far IR ($\omega < 800\text{ cm}^{-1}$) range. Along the chain c -axis, we can easily distinguish in both compounds a feature at about 650 cm^{-1} due to the overlapping of two modes. A rather sharp absorption at about 100 cm^{-1} and a peak at $735\div 750\text{ cm}^{-1}$ also characterize the spectra of both materials. The number of phonon modes increases considerably when the light polarization is oriented along the transverse direction (ab -plane). Besides many sharp

Table 1. Normal modes analysis of $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$, with X=Br and Cl.

Normal modes	Number of modes		Activity		
	Total	Acoustic	Optical	Raman	IR
A	16		16	aa+bb, cc	
B	16	1	15	aa-bb, ab	$E \parallel c$
E	17	1	16	aa, bc	$E \parallel a, E \parallel b$

Table 2. Resonance frequencies (ω_0^i) in units of [cm^{-1}] of the ω_{TO} phonon modes detected with light polarization $E \parallel c$, as determined from the Lorentz fit to $R(\omega)$.

$\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$	90.5	103.2	451.8	502.6	624.9	652.9	737.1
$\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$	97.1	131.0	452.4	562.8	649.6	665.1	746.8

Table 3. Resonance frequencies (ω_0^i) in units of [cm^{-1}] of the ω_{TO} phonon modes detected with light polarization $E \perp c$, as determined from the Lorentz fit to $R(\omega)$.

$\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$	50.9	69.0	81.4	106.8	117.7	145.1	178.2	205.5
	249.1	265.9	329.1	460.6	636.2	655.1	763.4	
$\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$	63.3	86.3	122.8	138.7	163.7	188.7	210.9	265.9
	308.3	342.1	483.9	654.0	670.3	771.9		

absorption lines recognized below 300 cm^{-1} , three dominant features can be identified within the ab -plane for both compounds at about 450 , 650 and 750 cm^{-1} . The peak at 650 cm^{-1} is also splitted in two distinct components, which are well resolved in the case of the Cl compound. The general trend of the phonon spectra indicates a softening of the modes in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ with respect to the Cl telluride. This is consistent with the 7% increase of the unit cell volume when Cl is substituted with Br (Refs. [3,6]). The larger Br ionic mass also leads to a further renormalization of the resonance frequency due to the change in the reduced mass within the harmonic approximation.

Only very weak deviations are observed in the spectra when the temperature is varied from 5 up to 250 K. The phonon frequencies for both compounds are slightly softening with increasing temperature. The shift is of the order of 1% and is likely to be attributed to anharmonic effects associated to the thermal expansion of the crystal. From 5 to 20 K (i.e., crossing the ordering transition temperature) no variation of $R(\omega)$ is observed within the instrument resolution, even in the presence of a magnetic field up to 7 T. At energies higher than 800 cm^{-1} (see inset of Fig. 2), structures may be identified at about 6000 and 30000 cm^{-1} for the Cl compound, while $R(\omega)$ of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ has less pronounced features.

3 Discussion

$\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ and $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ are isostructural compounds, crystallizing in the tetragonal structure with space group $\text{P}\bar{4}$ (Ref. [18]). The corresponding factor group is isomorphic to the point group S_4 . The unit cell is

made up of two formula units with eleven atoms each and therefore comprises 22 atoms. It is possible to distinguish between three inequivalent oxygen positions [5] (intratetrahedral O1, intertetrahedral O2, and O3), as shown in Figure 1. The site symmetries of the atoms in the unit cell are C_1 (4-Cu, 4-Te, 4-Br/Cl, 4-O1, 4-O2) and C_2 (2-O3). Group theoretical analysis permits to establish the number of the lattice vibrational modes and to determine their IR (and/or Raman) activity. Using the correlation method [21], and after subtracting the acoustic modes $B + E$, we have found for the total irreducible representation

$$\Gamma = 16A + 15B + 16E \quad (1)$$

corresponding to 47 Raman ($A+B+E$) and 31 IR ($B+E$) active modes. Because of the lack of inversion symmetry, certain modes ($B + E$) are in principle accessible to both techniques. The results of the group theoretical analysis are shown in Table 1.

A standard Lorentz phenomenological approach based on the classical dispersion theory has been applied to directly fit the $R(\omega)$ curves [19]. This allows to extract the resonance frequencies of the detected phonon modes. These frequencies, as obtained from the fit, are listed in Tables 2 and 3 for light polarization parallel ($E \parallel c$) and perpendicular ($E \perp c$) to the chains, respectively. From our reflectivity measurements we can clearly identify $7(E \parallel c) + 15(E \perp c) = 22$ phonon modes for the Br and $7(E \parallel c) + 14(E \perp c) = 21$ for the Cl compound. While the number of detected phonon modes within the ab -plane ($E \perp c$) is in good agreement with the normal modes analysis (Tab. 1), the number of observed phonons with $E \parallel c$ polarization is well below the group theoretical prediction ($B = 15$). The normal modes analysis

permits us to estimate only the number of expected IR active modes but gives no information on the related resonance frequencies nor on their oscillator strength. This means that some modes may be too weak to be detected or that two resonances may be too close to be resolved. A shell-model calculation is therefore necessary to resolve that issue.

The reflectivity of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ and $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ are well reproduced within the Lorentz phenomenological model. It is known however that asymmetric lineshapes (the so-called Fano lineshapes) are expected when a discrete state (lattice vibration) is degenerate with states belonging to a continuum which may be of electronic or magnetic nature [22]. Fano lineshapes have been detected in the infrared spectra of several SP compounds like TiOCl (Ref. [23]) and $\alpha\text{-NaV}_2\text{O}_5$ (Ref. [15]), as well as in some high-temperature superconducting cuprates [24,25]. The symmetric (Lorentz-like) lineshape of the phonon modes of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ and $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ is therefore suggesting a weak coupling of the lattice degrees of freedom with the underlying magnetic (and electronic) continuum.

The nature of the magnetic ordering phase transition in the $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ ($\text{X}=\text{Br}$ and Cl) is still unclear. As already mentioned, scenarios involving a structural phase transition have been put forward for both compounds [6,12]. A lattice distortion at the magnetic ordering transition temperature T_0 should therefore result in a shift of the phonon frequencies or even lead – if the symmetry of the lattice is reduced at T_0 – to the activation of new phonon modes. However, no shift in the resonance frequencies nor activation of new phonons were found in our $R(\omega)$ spectra while crossing T_0 and/or by applying a magnetic field. This result is consistent with the Raman measurements, where no phonon anomalies have been observed, as well [3,8]. The lack of signatures for a structural phase transition may be related to the small displacements of the atoms involved in the transition. Similar results were found by optical reflectivity and transmission measurements on CuGeO_3 , where only a few of the predicted SP-activated phonon modes were detected [16,20,26].

Band structure calculations within the local density approximation (LDA) predict the presence at the Fermi level of four half-filled bands with dominant Cu 3d character [5]. It is well known that the LDA approximation do not take fully into account the electronic Coulomb repulsion which is in fact shifting these bands. A Mott insulator characterized by a charge gap 2Δ between the lower and upper Hubbard bands [27] is therefore the expected scenario for $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ (Ref. [5]).

The $\sigma_1(\omega)$ curves (along the chain c -axis) obtained through KK transformations [19] are shown in Figure 3. For both materials, $\sigma_1(\omega)$ starts to increase at $\omega \approx 4000 \text{ cm}^{-1}$ and a peak at 6000 cm^{-1} is clearly present in the Cl compound only. We are tempted to attribute this peak to the electronic excitations across the Hubbard bands so that the maximum in $\sigma_1(\omega)$ at 6000 cm^{-1} can be associated to the effective Coulomb repulsion energy U (i.e., the energy difference between the peaks of the lower and upper Hubbard bands). If one assumes that the single-

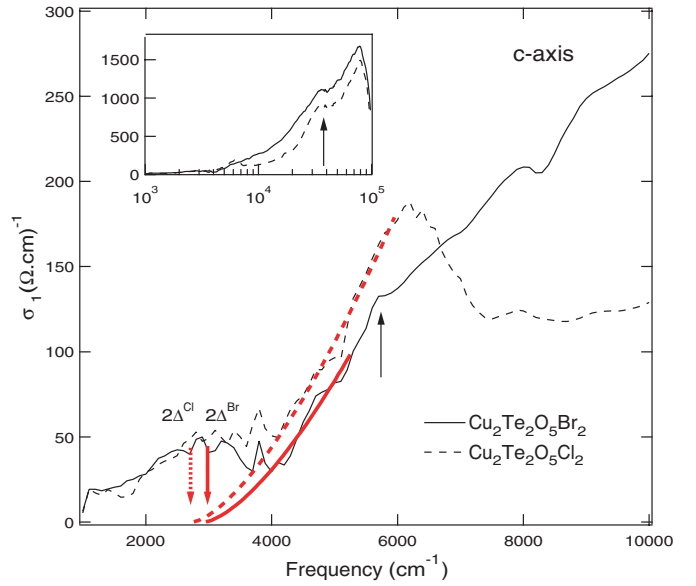


Fig. 3. Real part of the optical conductivity $\sigma_1(\omega)$ of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ and $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ along the chain c -axis as determined from the KK transformations. The thin up-arrow indicates the point at which $\sigma_1(\omega)$ changes its slope in the Br compound. The thick curves are fits of $\sigma_1(\omega)$ after equation (2). The energy gaps are indicated by the thick down-arrows. Inset: $\sigma_1(\omega)$ of the two compounds at high energies. The arrow indicates the electronic interband transition at 35000 cm^{-1} , which is broad in the Br compound.

particle densities of states rise as $E^{1/2}$ near the band edge, it is possible to determine the gap value 2Δ by fitting the $\sigma_1(\omega)$ onset with the formula

$$\sigma_1(\omega) = \sigma_0(\omega - 2\Delta)^{3/2}, \quad (2)$$

where σ_0 is a constant related to the average kinetic energy [28]. The extracted gap value is $2\Delta^{\text{Cl}} = 2740 \text{ cm}^{-1}$ for the Cl compound, with $\sigma_0^{\text{Cl}} = 9.83 \times 10^{-4} \Omega^{-1} \text{ cm}^{-5/2}$.

For the Br compound, no peak is observed at 6000 cm^{-1} in the $\sigma_1(\omega)$ spectrum, but just a change of slope at $\sim 4500 \text{ cm}^{-1}$. It might also be related to the excitation across the Hubbard gap. We suggest that in the Br case, the Coulomb repulsion is not giving the usual peak contribution to $\sigma_1(\omega)$ because of the screening effect due to the electronic interband transitions (see inset of Fig. 3). The absorption at $\sim 35000 \text{ cm}^{-1}$ is in fact much broader in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ with respect to $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$. Fitting the $\sigma_1(\omega)$ gap onset with (2) yields $2\Delta^{\text{Br}} = 2930 \text{ cm}^{-1}$ and $\sigma_0^{\text{Br}} = 8.82 \times 10^{-4} \Omega^{-1} \text{ cm}^{-5/2}$. The $\sigma_1(\omega)$ curves with light polarization within the ab -plane (not shown here) display the same features observed along the chain c -axis and are not discussed further.

We can finally comment on the absence of magnetic excitations in the $R(\omega)$ spectra of $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$. Magnetic excitations are in principle not IR active. However, they can under favorable conditions carry a finite electric dipole moment, as it has been demonstrated [15] for the $S = 1/2$ Heisenberg spin chain $\alpha\text{-NaV}_2\text{O}_5$. $\alpha\text{-NaV}_2\text{O}_5$

is a 1/4-filled two-leg ladder system with the d electron shared by two V ions in a V-O-V orbital along the rung. In such a system the effect of dimerization is to introduce a long range charge ordering with one electron per site on one single leg of the ladder. A spin-flip can therefore generate a repulsive interaction and push an electron (or more precisely, a portion of its wavefunction) on the other leg of the ladder, with an obvious modulation of the electric dipole moment [15,29]. A different kind of magnetic excitation has been observed in the La_2CuO_4 , Nd_2CuO_4 , Pr_2CuO_4 , and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ undoped copper oxides by IR transmission spectroscopy [13]. The presence of strong multimagnon sidebands in these compounds was explained by Lorenzana and Sawatzky [14] in terms of a phonon assisted activation of the electric dipole moment of a two-magnon excitation.

Several magnetic excitations, whose energy and intensity depend on temperature and on the applied magnetic field, were found in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ by Raman scattering experiments [6]. No trace of these excitations has been observed in our IR $R(\omega)$ curves. A possible explanation for this result may be that the observed Raman-active magnetic excitations do not generate any modulation of the electric dipole moment and are therefore undetectable by the IR experiment. The electric dipole moment modulation, realized in α' - NaV_2O_5 because of the charge ordered ladder structure, is not possible in $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$, where the tetrahedral basic cluster is composed by 4 singly occupied Cu^{2+} ions, and no charge ordering occurs. Similarly, the mechanism for the two-magnon excitation proposed for the undoped copper oxides can not be applied to $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$. In this model a crucial role is played by the displacement of the O^{2-} ions in the Cu-O planes. No O ion is mediating the Cu-Cu interaction in $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ and therefore the model does not apply to this class of compounds, consistently with the absence of sideband absorptions in our spectra. For the $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ case, the lack of IR signatures of magnetic excitations is less surprising: in fact no well-defined magnetic excitation has been observed by Raman scattering in this material [6]. The absence of sharp magnetic features in Raman spectra has been explained as being the consequence of the Cl large inter-tetrahedra coupling [3,10].

4 Conclusions

The nature of the magnetic ordering phase transitions of the $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ with $\text{X}=\text{Cl}$ and Br remains an unresolved issue. We provide here the first comprehensive study of the optical properties of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ and $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$, over a broad spectral range and as a function of temperature and magnetic field. We have been able to identify the characteristic energies of the IR active phonon modes and of the electronic gap. No frequency shift and no additional excitations have been observed while crossing the magnetic ordering transition temperature T_0 nor by raising the field. Moreover, there is not any optically allowed magnetic excitation below T_0 in our spectra, which could be considered as the IR counterpart

of the two-magnon pyramidal shaped feature and the longitudinal magnon mode seen in the Raman spectra [6]. Mechanisms as charged bi-magnons or phonon assisted multimagnon optical absorptions seem to be inappropriate for the title compounds. However, the Raman active excitation due to the longitudinal magnon mode was detected at 16.3 cm^{-1} , well below our low frequency experimental limit. The possibility for the presence of IR active magnetic excitations which might also well develop at frequencies lower than our experimental spectral range cannot be excluded a priori. While rather unlikely, this point deserves more experimental efforts in the microwave range and certainly calls for novel theoretical investigations.

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