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Phonon analysis of the $S = 1$ quantum spin systems $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ ($\text{X} = \text{Cl}$ and Br)

G Caimi¹, L Degiorgi¹, H Berger² and L Forró²

¹ Laboratorium für Festkörperphysik, ETH Zürich, CH-8093 Zürich, Switzerland

² Institut de Physique de la Matière Complexe (IPMC), EPF Lausanne, CH-1015 Lausanne, Switzerland

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Abstract

We report our investigations of the electrodynamic response of the $S = 1$ quantum spin systems $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ ($\text{X} = \text{Cl}$ and Br), which develop a magnetic ordered state below 30 K. We measure the optical reflectivity over a broad spectral range extending from the far infrared up to the ultraviolet. Besides identifying the electronic interband transitions, we primarily focus our attention on the lattice dynamics, emphasizing the phonon modes spectrum and its temperature dependence. Our findings do not reveal any direct link between possible structural anomalies and the transition into the magnetically ordered state at low temperatures.

(Some figures in this article are in colour only in the electronic version)

Low-dimensional quantum spin systems have attracted considerable attention over the past few years from both the theoretical and experimental points of view [1]. In these systems the long-range magnetically ordered phases (ferro- or antiferromagnetic) are suppressed by the effect of quantum fluctuations. There are various origins for quantum fluctuations: the reduced dimensionality of the investigated system (chains or layers), the small spin ($S = 1/2$ or 1) and/or the effect of magnetic frustration (competition between exchange processes). The interest in such phenomena has mainly been motivated by the investigation of the two-dimensional superconducting cuprates (HTC) as well as of related transition metal oxides. Very often the two-dimensional exchange topologies provide the basis for an effective interplay between competing interactions with remaining spin anisotropies. This leads to rich phase diagrams of short- and long-range ordered phases dependent on certain coupling parameters [1].

Several materials have been designed and developed so far as prototype examples of low-dimensional quantum spin systems. There has been much experimental activity directed at $S = 1/2$ materials involving Cu^{2+} ions with a $3d^9$ configuration, or Ti^{3+} and V^{4+} systems in the d^1 configuration. To give a few examples we start by mentioning the spin-Peierls CuGeO_3 system and the charge ordered NaV_2O_5 compound, representing the class of materials with broken translational symmetry [1]. Moreover, the two-leg spin ladder system SrCu_2O_3

and the chain/ladder $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ series [2] have been intensively investigated with respect to their spin and charge degrees of freedom, possibly representing a minimal model for underdoped HTC [3]. In this context, the layered TiOX ($X = \text{Cl}$ and Br) compounds [4, 5] were also considered to be most promising candidates for superconductivity based on dimer fluctuations [6]. Another synthesis strategy, that has proved to be quite successful, is the use of so-called lone pair cations such as Te(IV) and Se(IV) . In this respect, we mention first $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ ($X = \text{Cl}, \text{Br}$) [1, 8], because its unconventional magnetic ordering for the chlorine system, as well as $\text{Cu}_2\text{Bi}(\text{SeO}_3)_2\text{X}$, because of its $S = 1/2$ Kagome-type lattice [7].

The aim of our (optical) study is to search spectroscopically for new phases showing low-dimensional spin couplings between the magnetic ions in the system $\text{NiO-NiX}_2\text{-TeO}_2$ ($X = \text{Cl}, \text{Br}, \text{I}$). To our knowledge, only a few oxide phases have already been described containing Te(IV) in combination with Ni(II) : e.g. NiTe_2O_5 , $\text{Ni}_2\text{Te}_3\text{O}_5$. Two further new phases with the general formula $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ ($X = \text{Cl}, \text{Br}$), which are layered structures with two-dimensional arrangements of NiO_6 and NiO_5X octahedra and TeO_3 tetrahedra, have recently been discovered [9]. In such coordinations the $3d^8$ electron configuration of nickel(II) leads to well-localized $S = 1$ spins and a negligible or quenched orbital momentum. These $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ compounds are quite unexplored from both theoretical and experimental points of view. Nevertheless, they provide the possibility of comparing prototype $S = 1/2$ systems [1, 2, 4, 5, 8] with those characterized by the $S = 1$ state from the perspective of the absorption spectrum.

This novel 2D $S = 1$ quantum spin system $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ ($X = \text{Cl}, \text{Br}$) crystallizes in the monoclinic structure with space group $C2/c$, and shows a layered structure built up of corner-connected ($\text{Ni}_5\text{O}_{17}\text{X}_2$) entities, made of five Ni(II) octahedra associated by edge and face sharing. The Te(IV) atoms are fixed upon the nickel layers. Their lone pairs and the halogen atoms are packed in a double layer perpendicular to the (010) direction. $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ is furthermore characterized by an antiferromagnetic superexchange interaction [9]. The magnetic susceptibility as a function of temperature shows a Curie-Weiss behaviour with a negative Weiss temperature of roughly $\theta = -50$ K. There is also evidence for magnetic ordering phenomena occurring at transition temperatures, which vary with the interlayer separation: namely, $T_C = 23, 28$ and 30 K for $X = \text{Cl}, \text{Br}$ and I , respectively [9]. These T_C s also represent the onset temperatures for the divergence of the field-cooled and zero-field-cooled susceptibilities. These effects are attributed to random fields induced by spin canting [9].

In this short communication, we discuss the optical reflectivity ($R(\omega)$) spectra of $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$, measured on high-quality single crystals. Our specimens were synthesized by chemical transport reactions in sealed quartz glass tubes, as described in [9]. The obtained crystals have a shiny optical surface with a size of $5.6 \text{ mm} \times 6 \text{ mm}$ for $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{Cl}_2$ and $8 \text{ mm} \times 2 \text{ mm}$ for $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{Br}_2$. Our optical data were collected over a wide frequency range extending from the far-infrared (5 meV) up to the ultraviolet (10 eV). In the infrared spectral range we made use of a Fourier interferometer equipped with a magneto-optical cryostat, allowing the temperature to be varied from 2 to 230 K and a magnetic field up to 7 T to be applied. No magnetic field dependence is observed at any temperature, so that we will exclusively concentrate our attention on the temperature dependence of the absorption spectrum. In order to address any possible anisotropy in the electrodynamic response of the $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ systems, light was polarized within the (010) plane, either along the z (chain) or the x (transverse) direction. Both samples are platelet like, preventing any investigation along the y axis. Details pertaining to the experiment can be found in [10, 11].

Figure 1 illustrates the far-infrared optical reflectivity $R(\omega)$ from 0 to 0.1 eV at 10 K for both compounds and polarizations. Along each polarization direction, the $R(\omega)$ spectra for both compounds are rather similar, with an equivalent number of sharp lines (figure 1).

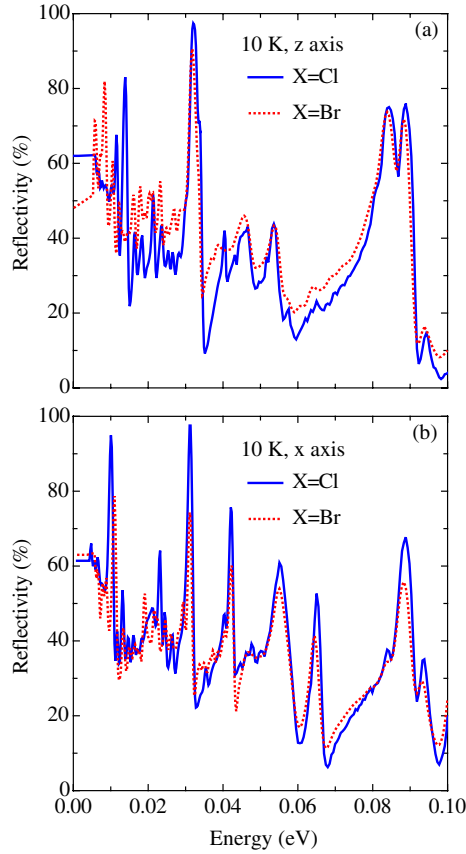


Figure 1. Reflectivity $R(\omega)$ of $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ measured at 10 K in the energy range characterized by the phonon modes. Panel (a) refers to the electrodynamic response with light polarized along the chain z axis, while panel (b) displays $R(\omega)$ along the transverse x axis.

The temperature dependence of $R(\omega)$ along the transverse x axis is displayed in figure 2(a). Besides a narrowing of the modes there is the appearance of a new feature at about 0.02 eV with decreasing temperature.

Measuring $R(\omega)$ over such a broad spectral range allows us to perform reliable Kramers–Kronig (KK) transformations [10, 11]. To this end, the experimentally measured $R(\omega)$ is extended below 5 meV with a constant term, because of the insulating nature of our compounds, while it is approximated at high frequencies with $R(\omega) \sim \omega^{-2}$ up to 2 eV and thereafter with $R(\omega) \sim \omega^{-4}$ to simulate the excitations into the continuum [10]. By means of the KK transformations, we calculate the real part $\sigma_1(\omega)$ of the optical conductivity, which represents the absorption spectrum. The whole $\sigma_1(\omega)$ spectrum at 10 K for light polarized along the transverse x direction is illustrated in the inset to figure 2(b) for the Cl compound. The low-frequency part of the $\sigma_1(\omega)$ spectrum in figure 2(b) is characterized by the vanishing of the optical conductivity in the dc limit. This underlines the insulating nature of the $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{Cl}_2$ system along the x axis. Even though it is not shown in this communication, the same is verified for the z axis in $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{Cl}_2$ and in $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{Br}_2$ for both polarizations.

At high frequencies $\sigma_1(\omega)$ is characterized by several absorptions at 0.36, 1.96, 5.5 and 7.4 eV. On the low-frequency side of the feature at 5.5 eV, there is a broad shoulder at about

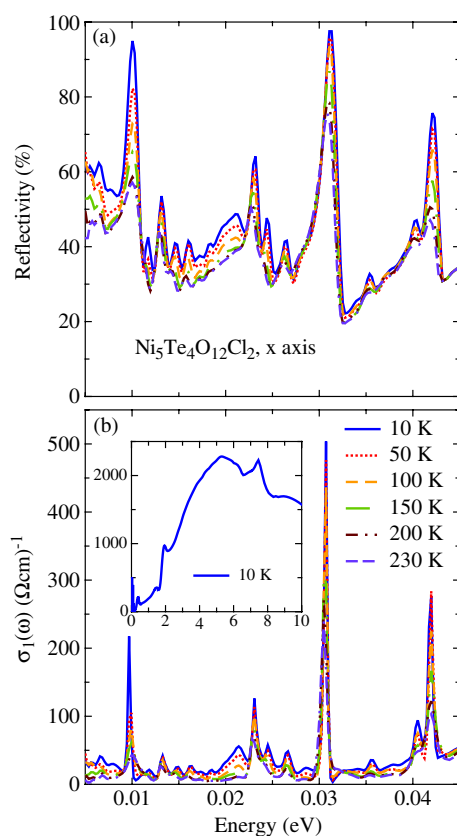


Figure 2. Temperature dependence of $R(\omega)$ in $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{Cl}_2$ with light polarized along the transverse x axis (a). The curves are plotted in the energy range (between 5 and 45 meV) where the temperature dependence is more pronounced. Panel (b) shows the corresponding $\sigma_1(\omega)$ curves. The inset illustrates the whole absorption spectrum up to 10 eV.

3.6 eV. These features are ascribed to the electronic interband transitions of the $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ system. A band structure calculation would be of great interest, in order to unambiguously identify these transitions. However, those calculations are not yet available in the literature. Therefore, we may just speculate that the Ni 3d bands lie around the Fermi energy. We further assume that, since the Ni atoms are embedded in an oxygen octahedra [9], a split of the 3d bands in a t_{2g} and a e_g complex occurs. Additional splitting due to lower symmetry, Jahn–Teller distortion or Hubbard repulsion cannot be excluded. The weak feature at 0.36 eV might thus be attributed to a (forbidden) transition in-between different 3d bands, since it is characterized by a low energy and relative weak intensity. On the other hand, the p bands of the other atoms (i.e. O, Te and Cl) are expected to lie far below the Fermi energy. The well developed absorptions at 1.96 eV might thus be assigned to a charge transfer from a p state (probably O 2p) into the Ni 3d. The other absorptions at 3.6, 5.5 and 7.4 eV are also generated by the interband transitions between low-lying oxygen p and Ni 3d states.

Our work is also motivated by the fact that the imprint of the magnetic phase on the lattice dynamics might shed light on the nature of the magnetic ordering phenomena at low dimensions. Therefore, the analysis of the phonon spectrum is of relevance. The reflectivity spectra, presented in figure 1, are dominated by an array of sharp absorptions, which indeed

Table 1. Summary of the expected IR and Raman active modes, compared with those detected experimentally.

	Predicted	Measured
Raman (xx, yy, zz, xy)	34	
Raman (xz, yz)	35	
IR ($x + y$)	33	18
IR (z)	33	14

originate from the lattice dynamics. The number of phonon modes expected in $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ crystals can be estimated by the space group analysis. The Bravais cell is composed of four $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ units with two lattice points. X-ray measurements unveiled the symmetry of each atom [9]: Ni has three different crystallographic sites Ni^1 (Wyckoff site 4e and site symmetry C_2), Ni^2 and Ni^3 (Wyckoff 8f and site symmetry C_1). Tellurium has two inequivalent sites (Te^1 and Te^2 , each with site symmetry C_1), while oxygen has six ($\text{O}^1, \dots, \text{O}^6$, each with symmetry C_1). The site symmetry for the 4X atoms is also C_1 . Applying the correlation methods [12], we may estimate the modes associated with each symmetry:

$$\begin{aligned}\Gamma^{C_2} &= A_g + 2B_g + A_u + 2B_u \\ \Gamma^{C_1} &= 3A_g + 3B_g + 3A_u + 3B_u.\end{aligned}$$

Summing up over the contribution of each atom and subtracting the acoustic modes (namely $\Gamma^{\text{acoustic}} = A_u + 2B_u$), one obtains for the vibrational modes:

$$\Gamma^{\text{cryst}} = 11\Gamma^{C_1} + \Gamma^{C_2} = 34A_g + 35B_g + 34A_u + 35B_u.$$

The modes A_u, B_u are infrared active (IR), while the others are Raman active:

$$\begin{aligned}\Gamma^{\text{IR}} &= 33A_u (E \parallel z) + 33B_u (E \parallel x, y) \\ \Gamma^{\text{Raman}} &= 34A_g (xx, yy, zz, xy) + 35B_g (xz, yz).\end{aligned}$$

In $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ along the x axis, we detect 18 modes at high temperature, which increase to 21 at low temperature. Along the z axis, we only observe 14 modes. The group theory result is summarized in table 1, where a comparison with the number of measured IR modes is displayed. The number of experimentally detected modes is less than the group theory prediction. Some of the modes might have the same excitation energies, so that they are not detectable separately. On the other hand, some modes might even have a weak dipole moment, below the detection threshold. The excitation energies of the modes in $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{Cl}_2$ approximately coincide with those in $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{Br}_2$ (figure 1), indicating that the phonon mode energies in $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$ are only marginally affected by the mass of the X atom.

We shall now address the temperature dependence of the optical spectra. In $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{Br}_2$ it turns out to be negligible and within the experimental error for both polarizations. On the contrary, $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{Cl}_2$ show a quite pronounced temperature dependence along the x axis, as shown in figure 2, while along the z axis it is more subtle. Our data unambiguously demonstrate an increase in the strength of the phonon mode for almost every phonon. Furthermore, new phonon modes appear by continuously lowering the temperature below 200 K. This is particularly true for the range between 19 and 25 meV for the x axis (figure 2). The mode at 10 meV is also of interest; it splits into two modes at 9.5 and 12 meV by lowering the temperature down to 10 K (figure 2). The appearance of new phonon modes as well as the splitting of some of them suggest changes in the lattice symmetry. This might well occur as the consequence of a lattice distortion. Symmetry breaking, leading to activation of silent or Raman

active phonons, may also explain the appearance of new infrared features, like in underdoped cuprates [13, 14] as well as in the ladder $\text{Sr}_2\text{Ca}_{12}\text{Cu}_{24}\text{O}_{41}$ [2] systems. Nevertheless, at present there is no low-temperature x-ray or neutron scattering experiment revealing the development of a lattice distortion and/or of a symmetry breaking. One might even try to find a link between the magnetic excitation and the lattice dynamics. Magnetic excitations are in principle not infrared active but can under favourable conditions carry a finite electric dipole moment [15–17]. Nonetheless, there is no evidence in $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{Cl}_2$ that changes in the lattice dynamics might originate from a phonon anomaly associated with the magnetic transition at T_C . Indeed, the temperature dependence of $\sigma_1(\omega)$ already develops at 200 K, well above T_C . This is quite different from the situation recently encountered in the spin-web Cu_3TeO_6 [18]. In this latter material a new mode was found to develop at temperatures lower than its Néel temperature. The origin of the temperature dependence in the lattice dynamics of the Cl compound therefore remains an open issue.

In summary, we have provided a far-infrared investigation of the phonon spectrum of $\text{Ni}_5\text{Te}_4\text{O}_{12}\text{X}_2$. We could detect some of the expected infrared active phonon modes and we have established a temperature dependence of the phonon spectrum along the x axis in the Cl compound. However, such a temperature dependence does not correlate with the onset of the magnetically ordered phase. In order to complement our infrared results it would be of great interest to approach this system from the perspective of other spectroscopies. More insight into the magnetic excitations and into the influence of magnetic ordering on the lattice dynamics can be gained by Raman spectroscopy and neutron scattering experiments.

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