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Temperature dependence of lattice contribution to dielectric response of francisite Cu₃Bi(SeO₃)₂O₂Cl (CBSCl)

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1. Introduction

Novel magnetic materials with frustrated geometries attract the attention of both theoretical and experimental communities due to their potential for supporting exotic emergent phenomena [1]. One example of such a crystal structure is a class of materials possessing a spin ½ kagomelike lattice – the so-called fransicites. The kagome geometry of corner-sharing spin triangles hosts a number of interesting properties. With nearest-neighbour antiferromagnetic (AFM) exchange interactions, the frustrated magnetic configuration prevents simple long-range magnetic order and leads to an infinitely degenerate classical ground state even at the lowest temperature when quantum fluctuations are included. This phenomenon is often referred to as a quantum spin liquid. In CBSCI, competing nearest-neighbour ferromagnetic interactions and next nearest neighbour AFM should lead to similar degenerate behaviour. However, considerable symmetric and antisymmetric exchange contributions act to lift the degeneracy stabilising a long-range antiferromagnetic order [2]. Presently the nature of these anisotropies and how they relate to the frustrated lattice are not well understood.

It is well known, that magnetic materials form the basis of modern electronics, information storage and processing. Scientists all over the world are focused on finding smart magnetic materials of the future, possessing entirely new magnetic behaviour and potentially beneficial properties. An example of this are frustrated structures supporting quantum spin liquid states, which may find applications in data storage and memory. In particular, the possibility to build so-called topological quantum computers based on these materials is widely discussed nowadays [3].

The improvement of microscopic magnetic models for francisites with kagome-like structure requires further experimental investigation. The present project work aims to contribute to the study of the interesting and so far only little investigated nature of kagome-like francisite Cu₃Bi(SeO₃)₂O₂Cl. Even though the unique magnetical properties of this material have not been addressed in this study, the nature of the low-temperature structural transformations and the general question about the possibility of an antiferroelectric phase are discussed. The nature of the structural transition occurring at 115 K and accompanying new phonon modes are of a particular interest for condensed matter scientists, as well as the relationship between these two phenomena.

Experience has shown that infrared spectroscopy is proving effective for the investigation of geometrically frustrated magnetic materials [4]. Therefore, the temperature dependent infrared reflectance spectra collected in this work provide a first look into the relationship between the AFM and electric degrees of freedom and represent a basis for further investigations.

2. About francisites

The signal crystal francisite, used in our studies, is a copper bismuth oxy-chloro-selenite originally discovered in natural South Australia iron deposits. A number of studies aimed at determining the single crystal structure were carried out yielding the composition and the stoichiometry of this material - the chemical formula is Cu₃Bi(SeO₃)₂O₂Cl [5,6].

The single-crystal structure of this compound is rather complex. At room temperature, it features orthorhombic Pmmn symmetry consisting of layers of corner sharing Cu^{2+} triangles, stacked along the c direction (Fig. 1). Each layer consists of buckled copper-oxide (CuO₄) square Kagome planes and SeO₃ trigonal pyramids. The magnetic cations build up a hexagonal cell within each layer. Buckling of the Cu²⁺ planes produces two inequivalent copper-ion sites (Cu1 and Cu2) possessing different oxygen bonding. This distinction will be significant for analysis of the phase transition. There is a weak interlayer connection by the Bi³⁺ and Se⁴⁺ bonds, halogen atoms are arranged inside the hexagonal cylinder made up by parallel stacking of the Cu²⁺ layers [7].

The class of materials which is now referred to as fransicites also include artificially synthesized $Cu_3Bi(SeO_3)_2O_2Br$ and $Cu_3Bi(SeO_3)_2O_2I$ i.e. $Cu_3Bi(SeO_3)_2O_2X$ (CBSX) where X is substituted by halogen ions.

Unlike the other francisites, CBSCI has an interesting feature, which is that one can observe phonon anomalies absent in the -Br and -I francisites. For example, the emergence of additional vibration frequencies by reaching a characteristic temperature, which led to the conclusion about possible onset of a phase transition and antiferroelectric nature of the low temperature structure [4].

As mentioned above, I have used infrared reflection spectroscopy to investigate the excitations in the Kagome-like lattice. A complete description of this technique is described in my previous bachelor thesis [8].



Fig 1. ab plane (a), ac plane (b), bc plane (c) and the projected (d) views of the $Cu_3Bi(SeO_3)_2O_2Cl$ crystal structure. The displacements of the low temperature antiferroelectric distortion are indicated in (b).

3. The phenomenon of antiferroelectricity

Antiferroelectricity (AFE) is a physical state, in which electric dipole moments (from the ions and electrons in the material) form an ordered crystalline array, with the polarisation directions of adjacent layers oriented antiparallel.

AFE often emerges by the onset of a phase transition at a critical temperature. In this case, the initial paraelectric cells become polarized, but with opposite dipole moments created in neighbouring cells, which cancel each other out resulting zero net moment.

From the microscopic point of view, antiferroelectrics can be divided into two basic classes with a displacement phase transition and transition of the type order-disorder. In the first case, in the crystal there exists an instability with respect to one of the lattice vibrations above the critical temperature. A lattice-dynamical treatment of displacive phase transitions leads naturally to the concept of soft modes, which was developed within condensed matter physics in the middle of the 20th century [9].

A soft mode refers to a certain phonon excitation, in which the frequency decreases with temperature change, i.e. the crystal softens against the corresponding displacements of the atoms by reaching the transition temperature. Phonon modes existing in the low-temperature phase soften completely at this point (their frequency reaches zero) i.e., they are no longer dynamical. In fact, the motions of atoms, determining the mode, transform into a static displacement pattern under the influence of an external thermodynamical force — which exactly describes the structure of another symmetry emerging upon the phase transition. It has to be noted, that this is not at all an obvious result, as the time scale of phonon frequencies corresponds to the THz range. Whereas, the lattice restructuration following the phase transition can take seconds. Such types of phase transitions, where atomic oscillations are parallel to the shifts that reorder the lattice are called displacive.

The second class of phase transitions of order-disorder type, are associated with dipoles, contained in polar crystals. While the temperature decreases, the dipole orientations, which were previously uncollinear due to the disordered thermal motion, gradually order and, finally, become spontaneously polarized in a more energetically favourable configuration. This occurs when reaching the transition temperature and is characterised by a rather sharp maximum of $\epsilon(T)$ that decreases with temperature increase [10].

4. Measurements and discussion

In the previous work room temperature reflectivity measurements were performed and by means of a Kramers-Kronig analysis, the phonon spectra of the parent Pmmn structure was investigated [8]. Observing the peaks in the imaginary part of the dielectric function, which describes the phonon response, we could identify some low-frequency phonon peaks, that seemed to be good candidates for soft modes which are believed to be associated with the structural distortion, leading to an antiferroelectric behaviour. The lowest-lying phonon modes for both crystallographic directions can be seen in the extracted dielectric response, shown in Fig. 2 (a,b) and Table 1.



Fig. 2 (a): Zoomed view of eps_1 ($\varepsilon_1(\omega)$) and eps_2 ($\varepsilon_2(\omega)$) for Cu₃Bi(SeO₃)₂O₂Cl along â axis.



Fig 2.b: Zoomed view of eps_1 ($\varepsilon_1(\omega)$) and eps_2 ($\varepsilon_2(\omega)$) for Cu₃Bi(SeO₃)₂O₂Cl along \hat{b} axis.

	E a	E b				
ν̃ [cm⁻¹]	ε΄΄ [1]	ν̃ [cm⁻¹]	$\varepsilon^{''}[1]$			
40	20	57	20			

Table 1: Numerical values of lowest laying phonon peaks for E//â and E// \hat{b}

In the course of this thesis we continued the reflectivity measurements and collected temperature dependent (12-300 K) reflectivity spectra on a single $Cu_3Bi(SeO_3)_2O_2Cl$ crystal in order to investigate the dielectric properties over a wide temperature range. We used a Bruker Fourier transform interferometer. The fundamental arrangement of the interferometer is described in my previous work [8].

The infrared (IR) reflectivity spectra are less accurate below 50 cm⁻¹; therefore the IR reflectivity spectra were combined with optimised spectra THz frequencies.

The results, obtained for both crystallographic directions, are shown in Fig. 3.



Fig. 3 (a): IR Reflectance of the $Cu_3Bi(SeO_3)_2O_2Cl$ single crystal for selected temperatures along \hat{a} axis.



Fig. 3 (b): IR reflectance of the Cu₃Bi(SeO₃)₂O₂Cl single crystal for selected temperatures along \hat{b} axis.

Because of a weak signal in the range between 0 and 20 cm⁻¹, the measurement quality is poor and thus no statements regarding the occurrence of phonon modes can be made in this region. Therefore, it was cut off in Fig. 3.

The resulting spectra in the range 20-600 cm⁻¹ can now be compared with those from reference [4] (Fig. 4). We can see a quite good overlapping of the phonon peaks with those from previous studies, which indicates the consistency of the measurements. The thin sample geometry (\approx 200 mm) results in strong interference fringes up to 450 cm⁻¹.



Fig. 4: The temperature-dependent reflectance spectra of $Cu_3Bi(SeO_3)_2O_2Cl$ along \hat{a} and \hat{b} axis [4].

Subsequently, we utilized the Kramers-Kronig transformation (described in detail in [8]) to obtain both the real and imaginary part of the complex dielectric function. The graphical representation is seen in Fig. 5 (a,b) and Fig. 6 (a,b). The ε_2 peak frequency data are summarized in Table 2 with assigned peak numbers in the far left column. The temperature dependence of phonon frequancies is also included (see Fig. 7 (a,b)). Error bars depicting the possible deviation of the measurement data are also included. The Error bars were determined by measurement of the peak widths.



Fig. 5 (a): eps_1 ($\varepsilon_1(\omega)$) for Cu₃Bi(SeO₃)₂O₂Cl along â axis.



Fig. 5 (b): eps_1 ($\epsilon_1(\omega)$) for Cu₃Bi(SeO₃)₂O₂Cl along \hat{b} axis.



Fig. 6 (a): eps_2 ($\varepsilon_2(\omega)$) for Cu₃Bi(SeO₃)₂O₂Cl along â axis.



Fig. 6 (b): eps_2 ($\epsilon_2(\omega)$) for Cu₃Bi(SeO₃)₂O₂Cl along \hat{b} axis.

	12K	20K	25K	30K	80K	110K	115K	120K	150K	200K	250K	300K
1	52.1	52.0	52.0	52.0	43.9	34.8	30.0	28.9	30.9	31.8	35.3	38.9
2	68.2	68.1	68.0	68.1	-	-	-	-	-	-	-	-
3	88.0	86.5	88.1	88.3	87.8	87.8	87.3	87.4	87.2	87.0	87.0	85.9
4	162.8	162.0	163.0	163.0	163.0	163.0	162.8	162.7	162.6	162.4	162.4	162.4
5	173.2	171.0	173.0	173.0	172.0	171.6	-	-	-	-	-	-
6	194.0	192.4	193.4	192.9	192.7	192.1	192.0	192.1	191.9	191.0	191.1	191.9
7	320.8	319.0	321.1	321.0	321.9	323.0	323.7					
8								326.5	326.0	324.9	324.0	323.4
9	332.0	330.0	331.9	332.1	330.4	329.1	327.6	-	-	-	-	-
10	564.4	560.1	561.9	560.4	559.0	557.3	556.2	555.2	553.2	551.1	549.4	548.7

Tab. 2 (a): Numerical values of phonon frequencies fo	r E//â in the temperature range 12 K-
300 K, [cm-1].	

Nº	12K	20K	25K	30K	60K	80K	110K	115K	120K	150K	200K	300K
1	35.3	35.0	36.1	36.8	37.0	37.4	38.0	38.0	38.0	41.7	43.8	48.7
2	66.9	67.0	67.0	67.5	66.9	67.0	67.0	68.0	68.0	68.0	67.0	67.0
3	114.0	114.0	113.0	114.0	114.0	113.9	114.0	114.0	114.0	113.9	114	113.9
4	186.0	186.0	185.9	185.1	185.0	185.1	185.3	185.5	185.4	185.0	184.9	184.0
5	458.3	458.2	457.8	457.9	458.2	458.2	457.9	457.9	457.2	457.9	456.8	455.6
6	487.1	487.3	486.9	486.9	486.9	487.1	488.1	488.2	-	-	-	-
7	511.0	511.1	511.1	510.2	510.0	509.0	508.0	507.6	507.4	506.2	504.1	503.7
8	544.1	544.0	544.0	543.5	543.6	543.6	543.9	543.9	543.9	543.0	542.5	541.2

Tab. 2 (b): Numerical values of phonon frequencies for $E//\hat{b}$ in the temperature range 12 K-300 K, [cm⁻¹].





Fig. 7 (a): Temperature dependence of transverse phonon frequencies, indicated in Table 2. (a) Appearance of several new phonons below 115 K is seen.



Fig. 7 (b): Temperature dependence of transverse phonon frequencies, indicated in Table 2.b Appearance of one new phonon mode below 115 K is seen.

As discussed above, we suspect the presence of certain deformation modes to allow a displacive phase transition. As described in the section "structure", halogen atoms in the room temperature structure are weakly bonded to the Cu2-cations and arranged at the centre of hexagonal cells, where large atomic displacements are possible due to a relatively large potential void. Referring to the paper of E. Constable [2], below the transition temperature magnetic correlations and thermal lattice contraction act on the Cl- and Cu2 ions, inducing energetically unfavourable conditions promoting a lattice distortion. Thus, the existence of these potential energy minima gives rise to the structure distortion at low temperature.

The atomic displacements represented in Fig. 1(b) result in the creation of local electric dipole moments within a single unit cell. The distortion results in polarisations vectors that are anti parallel and therefore one can imagine the structure consisting of two equivalent and opposed directed sublattices. Antiferroelectrics often tend to a doubling of the cell parameters when forming such a structure from the paraellectric phase, when the corresponding soft phonon modes display two different displacements, equal and opposite in magnitude [11,12].

Soft modes, as well as other oscillating modes of a crystal, are collective excitations and may disperse as a function of the wave vector q within the Brillouin zone. As stated above, a phase transition is characterized by freezing out of phonon modes i.e. $\omega(q)$ should approach zero frequency at some point in the Brillouin zone.

IR spectroscopic techniques can resolve only phonons at the Brillouin zone centre due to conservation of q-wavevectors for phonons and photons [13].

Let us suppose that the transition is driven by a zone boundary phonon (Z-Phonon). This soft mode cannot be IR active above the critical temperature (T_c) , but by reaching zero frequency the phonon branch will become "folded" to the new low-temperature zone centre. This leads to a doubling of the unit cell along one crystallographic direction. As the consequence of this multiplication of the unit cell, the previously unresolved mode may become IR active due to its different selection rules.

As we clearly see from the recorded spectra (see Tab. 2 and Fig. 7.), there are plenty of new phonon modes, arising in the infrared when approaching a temperature of around 115K, which then remain stable upon further cooling. This experimental evidence first allowed us to suggest the presence of a structural transition. The multiplication of the unit cell also provides a natural explanation to the presence of new phonon modes as an expansion of the unit cell will increase the number of normal modes it supports [2].

Proven by the studies of Prishchenko et al. [14] along with previous surveys including neutron and Raman scattering experiments ([15], [16]), the primary characteristic of the transition in CBSCI are additional atomic shifts of Cu2 and Cl atoms along the â crystallographic direction. Owing to the calculational methods, described in [14] one can make a conclusion, that a Z-distorted structure resulting in the doubling of the unit cell along the c-axis is, in fact, possible and would lead to the non-polar Pcmn space group. This is consistent with the increased number of phonons below 115 K.

The second type of transitions are those, which are caused by a zone-Center phonon (F-Phonon). Such modes have a common characteristic that they soften completely as the transition temperature is reached and then harden again below it [7].

A similar behaviour can be observed by a combination of the 1. phonon peak for $E//\hat{a}$ (see Fig. 7 (a))

It should be noted here that since the frequency of the soft mode is low and the intensity is high, observation of the soft mode by the traditional method of IR reflection is very problematic. This could explain the fact, that the frequency of the supposed Γ -Phonon practically never reaches zero.

An analysis of Prishchenko et al. [14] reveals that in case of a Γ -Phonon-driven phase transition, the symmetry of the structure changes to the polar P21mn group, and the inversion centre is lost.

To sum up, the strongest candidates for the new space group symmetry have proven to be the Pc21m and Pcmn space groups, where Cu2 und Cl ions displacements are opposite in

adjacent layers along the c axis but their direction are respectively contradirectional (Fig. 8 (a,b)). Both P21mn and Pcmn structures are generally consistent with the collected spectral data. However, a detailed diffraction analysis reveals that the Pcmn structure yield the best results with regard to energy minimisation for both Cl and Br compounds [2]. Its predominantly non-polar, antiferroelectric nature is also consistent with density-functional calculations (DFT) of lattice dynamics [14].



Fig 8: a) Single kagome-like layer in the $Cu_3Bi(SeO_3)_2O_2Cl$ structure. Bi atoms are omitted for clarity;

b) Right panel: atomic displacements in the adjacent layers upon the structural distortion. The red and black arrows are the displacements associated with the Γ - and Z-phonons, respectively [14].

To sum up, we have now established, that a displacement distortion caused by Z-Phonon (first Peak for $E//\hat{a}$) is most possible.

Transitions between the paraelectric and antiferroelectric states are of the second order nature. The characteristic feature of this transition type is the concept of *order parameter*, which continuously disappears when it comes to the transition. In the case of (anti-) ferroelectricity it is natural to choose the polarisation P as order parameter. When entering the ordered state, the symmetry of the system reduces. This phenomenon is called *spontaneous symmetry breaking* and is a general feature of all phase transitions.

In the case of a displacive phase transition, we can observe a soft mode, that softens when the temperature decreases and become broader. As the transition temperature is reached, the mode splits corresponding to the polarisation of the two sublattices in the AFE state. This behaviour is represented in Fig. 9.



Fig. 9: Helmholtz free energy as function of the order parameter P (polarisation) at a displacive phase transition.

At the transition of the type «order-disorder» an atom of the high-temperature unit cell may occupy either one of two shifted positions corresponding to the neighboring atoms. These two possible positions represent potential minima with a barrier in the middle between them and are energetically equivalent. At relatively high temperature the atoms are dynamically disordered among equivalent positions, i.e. there are highly aharmonic vibrations (hopping) and no long-range correlation. When it comes to transition the two potential voids become asymmetric i.e. the atom take up the preferable position and the whole system shows a regular pattern of atoms with long-range correlations. Fig. 10 represent the onset of a transition of the type order-disorder.



Fig 10: Helmholtz free energy as function of the order parameter P (polarisation) at a transition of the type order-disorder.

The phonon contribution to the thermal energy of a solid is distributed between all degrees of freedom, which are the phonons. The amplitude of a ε_2 -peak is roughly proportional to the spectral weight of corresponded phonon excitation. This means that in terms of amplitude we can evaluate how much the mode is populated i.e. density of states related to this mode.

In Fig. 11 (a, b), we plotted the amplitudes of a ϵ_2 -peaks for E//â and E//b against temperature. We can clearly see a massive increase in the spectral weight for the lowest frequency mode when temperature decreases. All other modes with higher frequencies are relatively stable over the whole temperature range.



Fig. 11 (a): Temperature dependence of of $\varepsilon_2(\omega)$ -amplitude for individual peaks along â axis.



Fig. 11 (b): Temperature dependence of of $\varepsilon_2(\omega)$ -amplitude for individual peaks along \hat{b} axis.

It makes sense to zoom the low-frequency spectral area to see more details:



Fig. 11: Zoomed view of eps_2 ($\varepsilon_2(\omega)$) for Cu₃Bi(SeO₃)₂O₂Cl along a â axis

In Fig. 11 we plotted the low temperature evolution of the complex dielectric function. At temperatures far above T_s one can observe a low-frequency peak, nearly disappearing on cooling until T_s . As $T \rightarrow T_s$ the intensity of this central peak increases, while its width decreases. By reaching the transition temperature its role is taken over by a soft mode, which hardens upon cooling. Such high temperature excitations are known as «*central modes*» and represent not an optical phonon, but a dielectric relaxation, which receives an oscillator strength from the coupled soft polar phonon and finally drives the phase transition.

Such behaviour represents a typical example of a commonly observed case of mixed displacive and order-disorder phase transitions [16].

Transitions of a mixed type depend on both the coupling energy between atoms and their vibrational energy. If the separating barrier between the energy minima is not very high a displacive transition type can also be presented.

As we know, an electric polarization appears when constituent ions are displaced from normal positions. This means, that a structural transition is associated with a typical anomaly of the dielectric permittivity. The dielectric constant rises to a high peak as the transition temperature is achieved. Fig. 12 shows $\epsilon(T)$ with a λ -shaped peak for Cu₃Bi(SeO₃)₂O₂Cl, where the static permittivity exhibits the Curie-Weiss like behaviour. This peak has a maximum at approximately 115 K, which coincides with the transition temperature.



Fig. 12: dielectric permittivity of Cu₃Bi(SeO₃)₂O₂Cl single crystals as function of temperature.

5. Summary and Outlook

This project work represents a survey of the structural phase transitions occurring at 115K and the nature of new phonon modes accompanying it.

After introducing some theoretical aspects concerning antiferroelectricity and material structure in this context, we presented the temperature evolution of phonon reflectivity obtained with a method of IR spectroscopy. The basis was my preliminary thesis [7], in which we performed reflectivity measurements at room temperature and revealed some phonon peaks to be good candidates to be a soft mode, associated with the displacive phase transition.

The emergence of new phonon modes (mostly for $E//\hat{a}$) below 115 K indicates an onset of a phase transition and could be explained by a zone boundary soft mode. However, no clear soft modes was found, which let us suppose that the nature of the structural transition may be of mixed displacive and order-disorder type. This is reflected in the fact, that our IR spectra revealed a low-frequency excitation, which is called a central mode and attributed to the lattice disorder caused by anharmonic atom vibrations. This central mode is also responsible for the strong dielectric anomaly in the paraelectric phase.

The anomaly of dielectric permittivity is reminiscent of an antiferroelectric transition. Our ϵ_1 calculations show a typical AFE response below 115 K [17].

6. References

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