

I thank Dr. Shuvaev for the review. In his review, there are more or less explicit assessments, suggestions or questions. I will try to address all of them:

- Suggestion related to Chapter 2: **This chapter gives a brief yet adequate description of the principal experimental methods used in the thesis. Some photographs or diagrams would be a worthy addition to aid in the descriptions of the different apparatus.**

I agree that some photographs or diagrams would be a worthy addition to aid in the descriptions of the different apparatus. Indeed, I provide photographs and descriptions of the setups I built by myself.

Firstly, I assembled a time-domain THz spectroscopy setup based on Teraflash spectrometer [J. Infrared Millim. Terahertz Waves **35**, 823–832 (2014)] (Ref. 143 in the thesis), allowing to exchange receiver and emitter antennas, whereby allowing to measure the directional dichroism as it is defined. The setup is displayed in Figure 1.

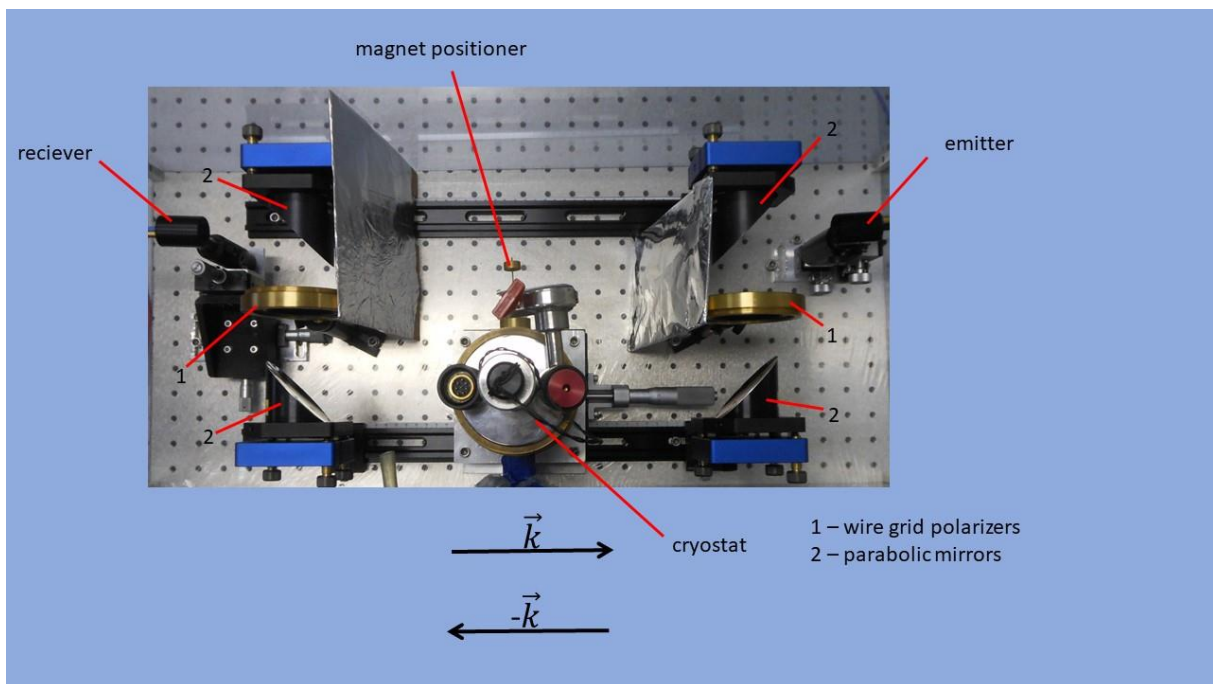


Figure 1: THz spectroscopy setup I aligned at Budapest University of Technology and Economics, allowing to exchange the emitter and the receiver, whereby allowing to measure the directional dichroism as it is defined: The light can propagate in one ( $\vec{k}$ ) or opposite ( $-\vec{k}$ ) direction. Different components of the setup are marked.

Secondly, I assembled the setup for measuring quasi-static magnetoelectric effect by the modulation technique, depicted in Figure 2. This setup is designed in the way to allow illuminating the sample from both sides in the direction perpendicular to both applied electric and magnetic field.

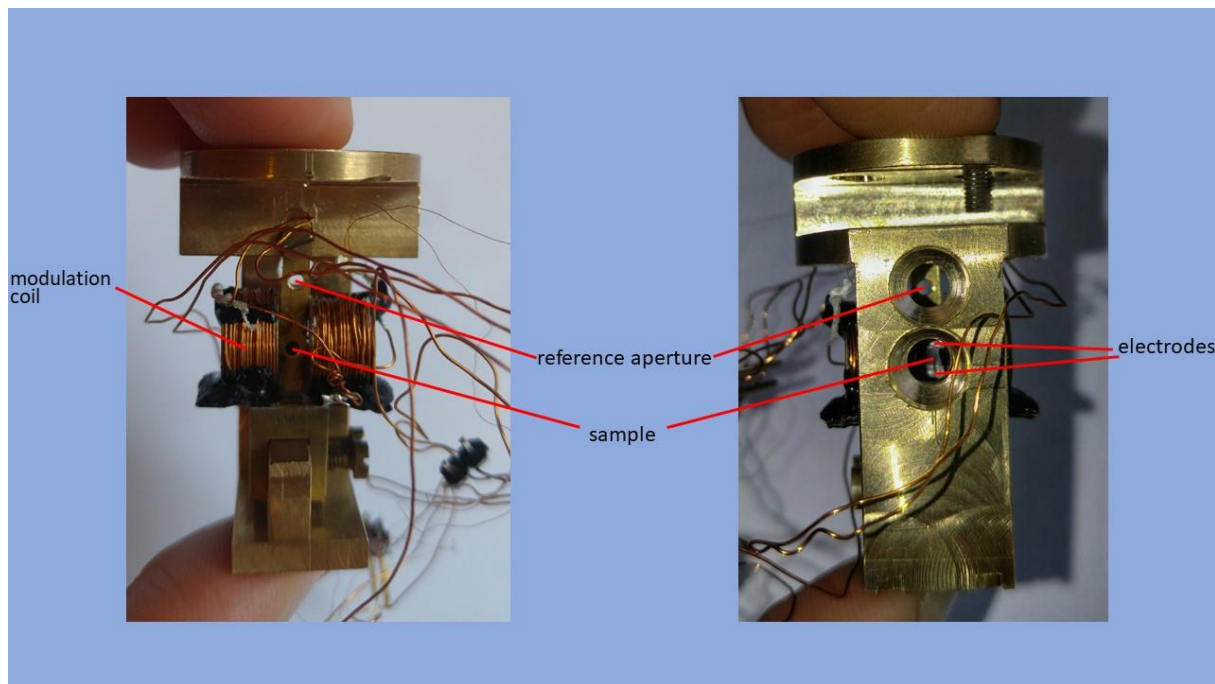


Figure 2: The setup for measuring quasi-static magnetoelectric effect by the modulation technique, photographed from opposite sides. Different components of the setup are marked.

- **Equation (2.2) is missing a square.**

Yes, it is true. I admit this mistake.

- Suggestions and series of questions related to Chapter 4: **It would be a nice addition to see plots of the peak position, spectral weight and damping as a function of temperature so that the profiles can be easily observed and compared with the static measurements and emergence of the different magnetic phases. This would be particularly interesting for the double peak structure of the electro-magnon in Y-hex. It seems that under field the two peaks have a slightly different dependence. Is this true? Could the two peaks be coming from different modulations of the magnetic structure i.e. a mix of TC and ALC or TC with an extra longer-range modulation on top?**

The reasons why I did not plot temperature dependence of the peak positions, spectral weight and damping as a function of temperature are following: 1) It does not bring too much new information in contrast to field dependence of the spectral weight, displayed in Fig. 4.3c in the thesis. 2) Transmission signal of the Y-hexaferrite  $\text{BaSrCoZnFe}_{11}\text{AlO}_{22}$  single crystal was too low in THz spectra below 150 K, therefore the spectral weight at low temperatures and low magnetic fields could not be determined precisely. 3) In zero magnetic field, the double-peak structure cannot be easily resolved, since it appears clearly only in field range 0.25-0.5 T, as seen in Fig. 4.5b in the thesis. To demonstrate this, in Figure 3 I plot the above-mentioned quantities taken from Raman spectra, in which the signal is sufficiently high. One can see trends which are obvious already from simple look at the spectra.

The spectral weight of the electromagnon (Figure 3b) could be in principle correlated with the static polarization, as it was done in the case of Z-hexaferrite  $\text{Ba}_{0.5}\text{Sr}_{2.5}\text{Co}_2\text{Fe}_{24}\text{O}_{41}$  [Phys. Rev. Lett. **120**, 027202 (2018)] (Ref. 208 in the thesis), but I did not measure the static polarization because the sample was leaky at temperatures above 100 K.

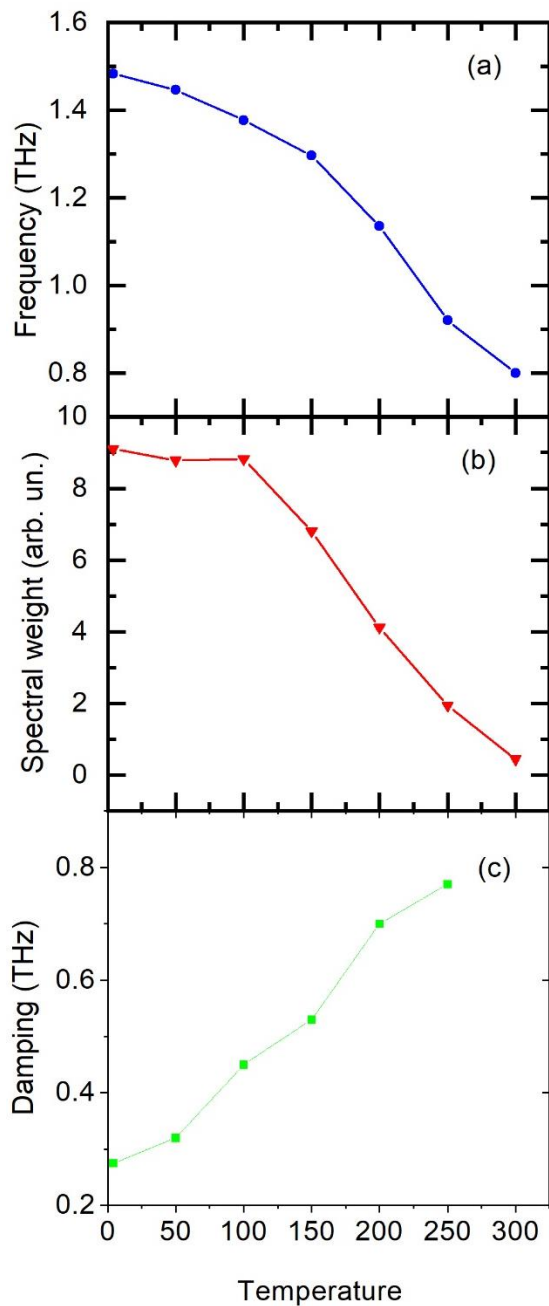


Fig. 4.4c from the thesis:

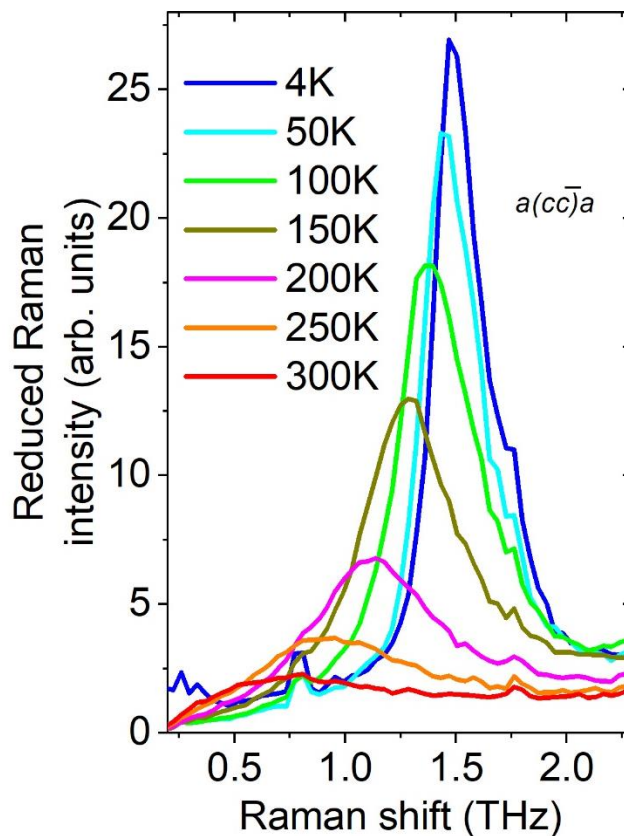


Figure 3: Temperature dependence of (a) frequency, (b) spectral weight and (c) damping for the electromagnon in Y-hexaferrite  $\text{BaSrCoZnFe}_{11}\text{AlO}_{22}$  single crystal. The data were evaluated using Raman spectra from Fig.4.4c in the thesis, which is displayed on right.

As regards to the different field dependence of the two peaks. I comment on the second peak in the thesis like this (page 79):

Let me yet comment on the high-frequency part of the doublet in the 2-fan structure, i.e. the narrow peak at  $\sim 1.5$  THz in Fig. 4.5(b), seen in the range from 0 T to 0.75 T and observed the most clearly at 0.25 T. This feature is not seen in the ZFC spectra plotted in Fig. 4.4(a,b), and it is weak at zero field at 150 K, where the ALC structure can be present beyond the 2-fan structure. Since it abruptly appears when 0.25 T is applied, whereby stabilizing the 2-fan state, it should be connected with the 2-fan state, but not with the ALC one. Note that it disappears below 1 T, i.e. at much lower fields than the main, broad peak. This may be connected to different conical angle dependence for small and large spins: One mode possibly involves deviations  $(\delta S_i^S)_x$ , thus its strength is proportional to  $\sin(\theta^L)$ , while the other mode involving  $(\delta S_i^L)_z$  is proportional to  $\sin(\theta^S)$ . Nevertheless, these are just speculations, while these features may be related to the physics beyond the model.

Thus, the answer is yes – the two peaks could be coming from different modulations of the magnetic structure: The second peak is related to the TC (2-fan) structure, while the main peak is present in both ALC and TC structures.

As regards to the suggestion that one of the peaks may be connected to TC with an extra longer-range modulation on top: 2-fan (TC) structure is commensurate and there is no extra modulation reported. Because of magnetic anisotropy, additional modulations of TC structures are improbable: While the in-plane helical modulation of the ALC structure does not increase magnetic anisotropy energy, any modulations of the TC structure would require magnetic anisotropy energy.

- Question and suggestion about magnetic frustration in hexaferrites: **The frustrated magnetic structure is mentioned a few times. Is this geometric or exchange driven frustration? A diagram showing the frustrated geometry would be nice to see.**

Ultimately, the magnetic frustration is always exchange driven, but in hexaferrites, it can be called as the geometric frustration: Nearly all nearest neighbor superexchange interactions are antiferromagnetic, but due to geometric reasons, not all neighboring spins can be aligned antiparallely.

I did not plot any diagram showing the frustrated geometry because such details of the magnetic structure were not subject of the thesis (I used the spin-block approximation), and describing such details is not straightforward. I am going to display a diagram showing the frustrated geometry here. Before, let me recall some basic rules for superexchange interactions. In the thesis, I write (page 59):

Due to crystal structure complexity, it is often difficult to estimate magnetic structures. Microscopically, the basic interaction is the Fe-O-Fe superexchange, which varies with the bond angle: It is strongly AFM for angles close to  $180^\circ$  and weakens with decreasing bond angle [184, 185]. Such a rule provides a rough guideline for magnetic structure estimation, however, the situation is complicated because exchange interactions occur via multiple paths.

There is yet a second, obvious rule – exchange interactions are stronger for shorter bond due to larger wavefunction overlap.

Knowing these rules, I can give an example of the frustrated geometry, which is quite simple since multiple-path exchange interactions are not considered. For demonstration, I picked Y-hexaferrite  $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ , which is a broadly studied compound. In Ref. [J. Phys. Soc. Jpn. **76**, 3, 034704 (2007)] (Ref. [185] in the thesis), they studied superexchange interaction in this compound by neutron diffraction.

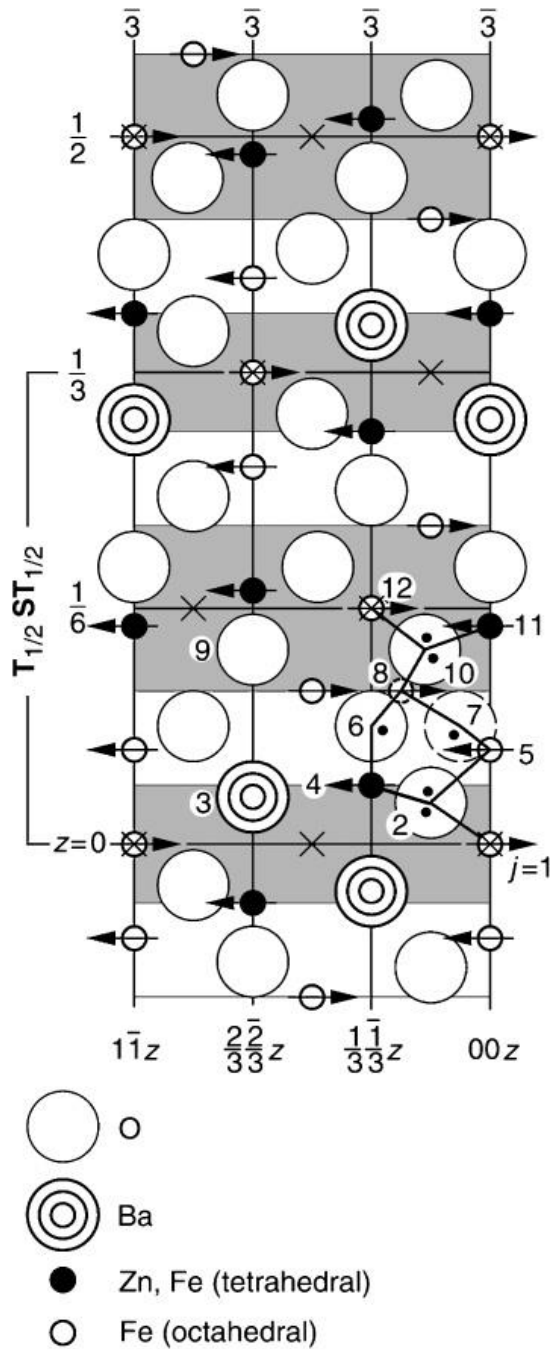
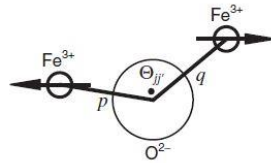


Fig. 1. Cross-section of the  $x = 0$  crystal  $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  with the  $c$ -axis being vertical,<sup>3,4)</sup> where  $z = 0, 1/6, 1/3,$  and  $1/2$  shown on the left are the coordinates along the  $c$ -axis. Drawn vertical lines are the triad axes. Cross indicates a center of symmetry. Layer numbers of  $j = 1$  to 12 are given to the ions ranging from  $z = 0$  to  $1/6$ . Arrows indicate the ferrimagnetic configuration of Fe magnetic moments, which are all parallel to the  $c$ -plane.<sup>4,9)</sup> Six superexchange interactions Fe(1)–O(2)–Fe(4), Fe(4)–O(2)–Fe(5), Fe(4)–O(6)–Fe(8), Fe(5)–O(7)–Fe(8), Fe(8)–O(10)–Fe(11), and Fe(11)–O(10)–Fe(12) are represented by two connected heavy lines with a dot indicating the angle between them, where numerals denote the layer numbers.<sup>4,8,9)</sup> Shaded portions indicate two types of ferrimagnetic bunches: one is composed of the Fe(1)- and Fe(4)-magnetic moments, and the other of the Fe(8)-, Fe(11)-, and Fe(12)-magnetic moments as will be discussed later (see §3.2).

In Figure 4, the frustrated geometry is shown, and in Table 1, parameters related to superexchange interactions are displayed. All displayed interactions are antiferromagnetic, but due to the geometric frustration, not all of them can be fulfilled. As a result, Fe(4) and Fe(5) are not aligned antiparallelly, because Fe(4)-O(2)-Fe(5) superexchange interaction is the weakest due to the smallest bond angle (113°) and quite large bond distance O(2)-Fe(5), reaching 2.33 Å. Based on ratio of Ba and Sr, Fe(4) and Fe(5) are aligned parallelly, giving rise to collinear ferrimagnetic structure, or they may have a general angle, giving rise to a helical structure. Therefore, Fe(4)-O(2)-Fe(5) bond lies on the boundary of the spin blocks.

Table 1: Table III in Ref. [J. Phys. Soc. Jpn. 76, 3, 034704 (2007)] (Ref. [185] in the thesis). Ref. [10] is [J. Phys. Soc. Jpn. 70, 2724 (2001)] and Ref. [11] is [Appl. Phys. 7, 227 (1975)]

Table III. Superexchange interactions for the  $x = 0$  crystal  $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  assuming that the lattice constants are  $a = 5.878 \text{ \AA}$  and  $c = 43.584 \text{ \AA}$ .



Configuration	Bond distance (Å)		Angle $\Theta_{jj}$ (°)	Exchange integral <sup>a)</sup> $J_{jj}$	Strength <sup>b)</sup>
	$p$	$q$			
Fe(1)–O(2)–Fe(4)	2.01	1.90	165		Very strong
Fe(4)–O(2)–Fe(5)	1.90	2.33	113	–0.365	Weak
Fe(4)–O(6)–Fe(8)	1.80	2.06	123	–0.503	Medium
Fe(5)–O(7)–Fe(8)	1.95	1.97	128	–1	Strong
Fe(8)–O(10)–Fe(11)	2.08	1.89	122		Medium
Fe(11)–O(10)–Fe(12)	1.89	2.02	124		Medium

a) Normalized by  $|J_{58}|$ .<sup>10)</sup>

b) Based on the calculation by Albanese *et al.*<sup>11)</sup>

- Question and suggestion about polar phonon shift in a Z-hexaferrite: **Could the shift in the polar phonon mode observed in the ceramic z-hex sample be due to strain? If the small crystallites of the ceramic are under strain this might explain the small observed change in electric polarisation compared to the single crystal data from the literature.**

This question probably refers to Fig. 4.7a,b in the thesis, where temperature-dependent THz spectra of Z-hexaferrite ceramics  $(\text{Ba}_{0.2}\text{Sr}_{0.8})_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$  and single crystal  $(\text{Ba}_{0.5}\text{Sr}_{0.5})_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$  are displayed. (Note that the abbreviation “z-hex” is used in Chapter 5 only, referring to Z-hexaferrite ceramics  $(\text{Ba}_{0.2}\text{Sr}_{0.8})_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ .) While the nonmagnetic excitation (possibly polar phonon) reaches frequency 1.374 THz in the ceramics, it reaches frequency 1.325 THz in the single crystal (at 7 K). Note that both ceramics and single crystal data were measured by myself, and there is no comparison of the data to literature.

To answer the question: I think that the difference in the excitation frequency can be simply ascribed to different chemical compositions of the ceramics –  $(\text{Ba}_{0.2}\text{Sr}_{0.8})_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$  – and the crystal –  $(\text{Ba}_{0.5}\text{Sr}_{0.5})_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ . Since the crystal contains more Ba compared to Sr with respect to ceramics, lower frequency of phonons involving Ba/Sr site motions is expected in the crystal. This is consistent with my observations. Different strain in different crystallites may be rather responsible for broader phonon peak (i.e. higher damping) in the ceramics compared to the single crystal, which I also observed.

- Questions about my perspective related to studying THz nonlinearities in magnetic systems, based on unsuccessful study of THz nonlinearities in hexaferrites. **What are the best systems to look at and how should the data be analysed?**

The first question is extremely broad and who knows the answer will for sure publish in highest-impact journals. Let me then specify the question to: What are the best magnetic systems for observing large nonlinearity in time-domain THz spectra? Following the thesis, the most important requirement is high enough light-matter interaction strength. If the aim was to switch between two (meta-)stable states, then low magnetic anisotropy, thus closeness to some instability, would be the second important requirement. Instead of further speculation, I give a reference to a recent perspective on this topic: [Appl. Phys. Lett. **120**, 050501 (2022)]

Second question can be specified to analysis of time-domain THz spectra. In the thesis, I cite an example of use of 2D THz spectroscopy: [Phys. Rev. Lett. **118**, 207204 (2017)] (Ref. [241] in the thesis), which is an elegant way how to deal with THz nonlinearities. Note that the main difference is much higher SNR of their table-top setup compared to the accelerator-based sources which I used in the thesis. Note however that 2D THz spectroscopy can be well used only for long-lived states, otherwise there will be no benefits of long delays between the two pulses and Fourier transform would have to be taken only for short time, which would limit the frequency resolution.

If the second question is taken more generally, I propose pump-probe experiments as optimal ways of investigating nonlinearities, as mentioned in the thesis.

- Question about optical properties of studied hexaferrites: **I wonder what the optical properties of the samples are under to assess if such measurements are feasible. Would the sample transmit optical frequencies for example?**

All studied hexaferrite samples were opaque for a naked eye. My coworkers tested that there is no transmission signal for 800 nm laser for Z-hexaferrite ( $\text{Ba}_{0.2}\text{Sr}_{0.8}$ )<sub>3</sub>Co<sub>2</sub>Fe<sub>24</sub>O<sub>41</sub> ceramics. Band gap of hexaferrites sensitively depends on chemical substitution (see for example [Results in Physics, **13**, 102244, (2019)]). I do not know optical properties of studied hexaferrites, but probably NIR (or even MIR) probe would have to be used in order to reach transparency region.

- My comment on the following sentence, related to Chapter 6: **A thorough analysis of obtained results has lead to the conclusion that the extrinsic effects are responsible for the observed THz poling.**

Based on this statement, I realized that my message about the analysis of the light poling was possibly not fully conveyed, and my choice of the term extrinsic when describing the effect was misleading. I wrote the thesis in a chronological and honest way, mentioning what was originally expected and that results were different. This probably made the story too complicated.

In conclusion, the heat flow, coming from the heat gradient causes the effect of poling. The heat gradient was caused by extrinsic sample geometry, but the effect itself is not extrinsic (I ruled out the possibility that it is caused by defects). Similarly, Seebeck or Peltier effects include temperature gradient, thus sample inhomogeneity, but they provide information on fundamental material properties, and not considered as extrinsic effects. Another example of an effect involving sample inhomogeneity is the flexoelectric effect, involving strain gradient.

The effect I observed is probably connected to the magnetoelectric anisotropy in diffusive transport [Phys. Rev. Lett. **94**, 016601, (2005)], (Ref. [82] in the thesis), which I also mentioned in the thesis.