Republic of Serbia
MINISTRY OF SCIENCE,
TECHNOLOGICAL DEVELOPMENT AND INNOVATION

Raman spectroscopy as a tool for studying spin-phonon coupling in multiferroic nanomaterials

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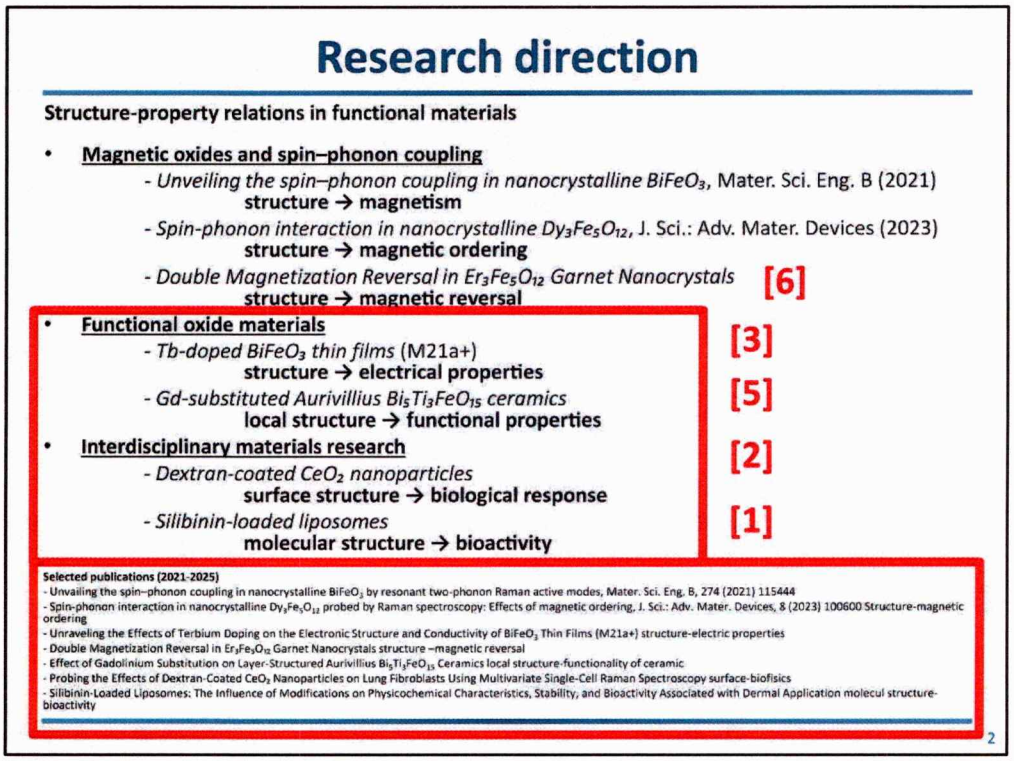


My research is focused on structure-property relations in functional materials. Using Raman spectroscopy and complementary techniques, we study how structural changes influence magnetic, electronic, and even biological properties of different systems. Regarding the CeO2 nanoparticles, I conducted porosimetry (BET) measurements to define surface area and porosity. When biological and spectroscopic data showed discrepancies in cellular response, my analysis of active site accessibility provided the missing link. I established a **quantitative correlation** between the physical properties of the material and its biological impact, which was essential for the overall reliability of the study.

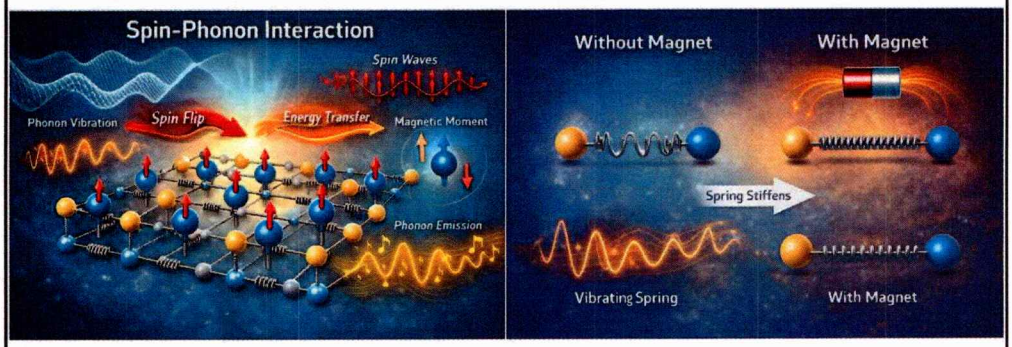
For the Gd-substituted Aurivillius ceramics, I introduced Raman spectroscopy as the central experimental technique. Conventional X-ray methods were not sensitive enough to detect the subtle local structural changes. My expertise allowed us to identify shifts in lattice symmetry and bond interactions that were previously inaccessible. This provided the definitive proof of how Gadolinium ions influence the functional properties of the ceramic.

I applied advanced Raman spectroscopy to resolve molecular interactions and the stability of silibinin-loaded liposomes, providing critical physical-chemical insights for dermatological application.

In all cases, my contribution went beyond data collection; I was actively involved in designing the experimental approach and interpreting the results, which directly led to the successful publication of these findings in high-impact journals.

Introduction – Motivation

- Magnetism and lattice vibrations in a material appear as completely separate phenomena…
- …but in some materials, they are directly linked.
- The question is: can we "see" magnetism through lattice vibrations?



Focus of this talk

- Spin-phonon coupling in magnetic oxides
- Raman spectroscopy as a probe of magneto-structural interactions
- Examples from rare-earth iron garnets and $BiFeO_3$ systems

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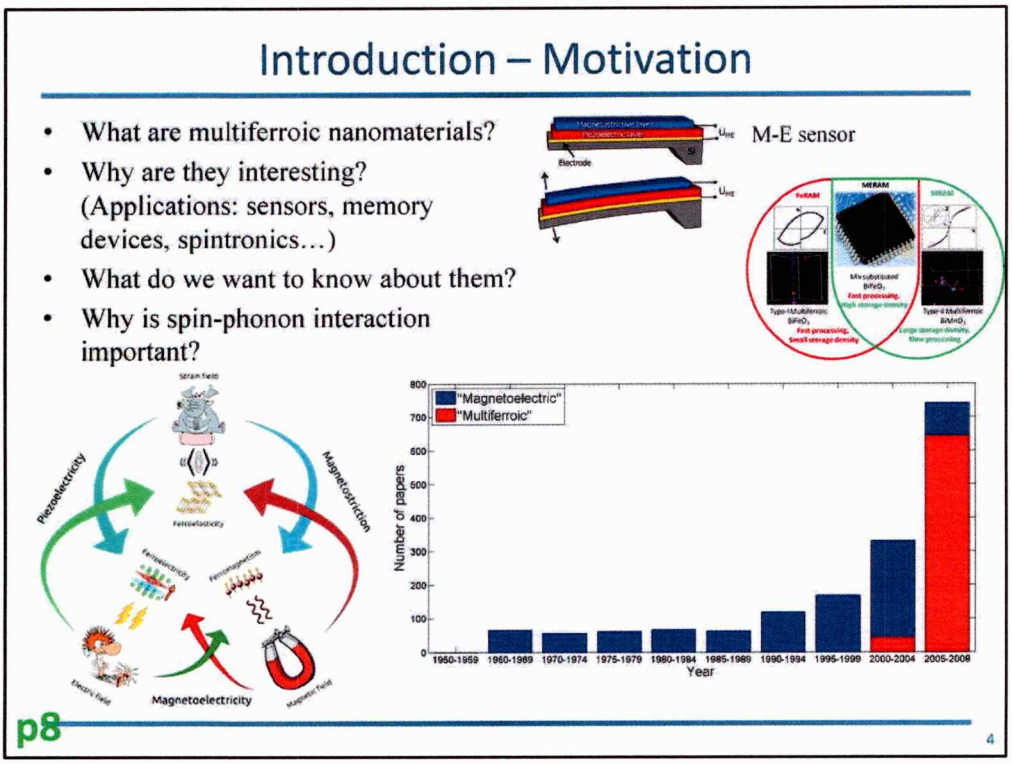


Multiferroic materials are materials that simultaneously exhibit **more than one ferroic order**, typically **ferromagnetism** (spontaneous magnetic ordering) and **ferroelectricity** (spontaneous electric polarization), sometimes also **ferroelasticity**. This coexistence allows **coupling between magnetic and electric properties**, which is rare in conventional materials.

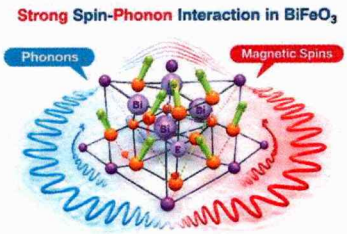
They can be used in **sensors** (detecting magnetic or electric signals), **memory devices** (storing information via electric or magnetic states), and **spintronics**, where the electron's spin, rather than its charge, is used to process and store information more efficiently.

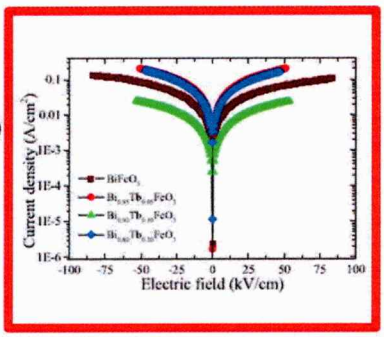
The increasing number of publications in recent years highlights that this is an **active and rapidly growing research field**.

Magnetoelectric interaction:
Combines **electronic & magnetic properties**
Enables **current-free devices** (e.g., non-volatile memory)
Can **revolutionize computing & communications**

Why $BiFeO_3$?

- Multiferroic at room temperature!
  - $T_C \approx 1100$ K (ferroelectric)
  - $T_N \approx 640$ K (antiferromagnetic)
- Scientifically important
  - Strong spin-lattice interaction
  - Applications: spintronics and memory devices
  - Magnetoelectric coupling
- Challenges: [3]
  - High leakage current
  - Presence of oxygen vacancies (Fe^{2+}/Fe^{3+})
- Why I study it:
  - Ideal for investigating spin-phonon interaction
  - Raman spectroscopy is sensitive to both lattice and magnetic effects





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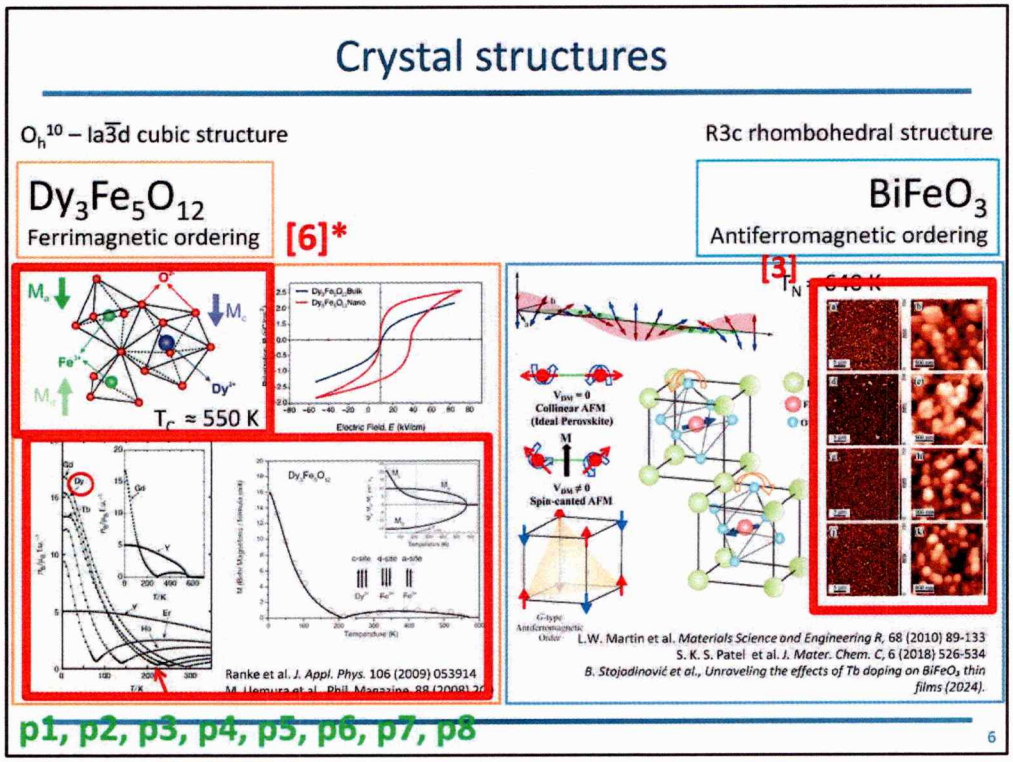
- Let's look at the fundamentals: BiFeO3 is a unique multiferroic at room temperature. Note the high transition temperatures TC at 1100 K and TN at 640 K which make it a prime candidate for practical applications.

- The importance here lies in the strong spin-lattice interaction and magnetoelectric coupling. These properties are the key to developing next-generation spintronics and advanced memory devices.

- However, we face two major bottlenecks: the **high leakage current** and the **presence of oxygen vacancies**. These defects, specifically the Fe^{2+}/Fe^{3+} fluctuations, are exactly what my research aims to solve.

Now, look at the graph in the right side, which is the core result of my paper **in Applied Surface Science, where I am** presenting influence of doping on current density profiles for, in our case, Tb-doped films. Observe how the 10% Terbium doping (the green curve) drastically reduces the leakage current by several orders of magnitude compared to the pure sample.



- Unit cell contains eight formula units with 160 atoms. Dy is in the dodecahedral sites with 8 oxygen ions, Fe is in tetrahedral and octahedral sites. Dy3Fe5O12 is ferrimagnetic material in nature with three magnetic sublattices.

- Fe ions are strongly coupled via antiferromagnetic superexchange interaction, resulting in a net moment of 5 μB per molecule at 0 K.

- The Dy sublattice couples antiferromagnetically with the net moment of the Fe^{3+} sublattices.

- At low temperatures the magnetization of Dy sublattice overrides the magnetization of Fe sublattices. With increasing temperature, the magnetization of Dy sublattice falls off more quickly than that of Fe sublattices and at compensation temperature (T_{com}) around 230K, the magnetizations of Dy and Fe sublattices are compensated. Above T_{com}, up to the transition temperature T_C = 550K, the magnetization of Fe sublattices predominates.

- Sharing the same crystal structure as DyIG, my comparative research on **Erbium Iron Garnet** reveals a unique **double magnetization reversal** not seen in the other systems. Unlike standard garnets, ErIG nanocrystals exhibit two compensation points during cooling, where the magnetization switches from positive to negative at 75 K and then reverts to positive at lower temperatures. These findings, including a complex **double-umbrella** spin structure at low temperatures, demonstrate that ErIG offers superior flexibility for designing advanced spintronic devices.

Canted antiferromagnetic ordering can be visualized as a **spin cycloid**, where the magnetic moments are mostly antiparallel but **slightly tilted (canted)** relative to each other. This canting leads to a **small net magnetization**, giving rise to **weak ferromagnetism**.

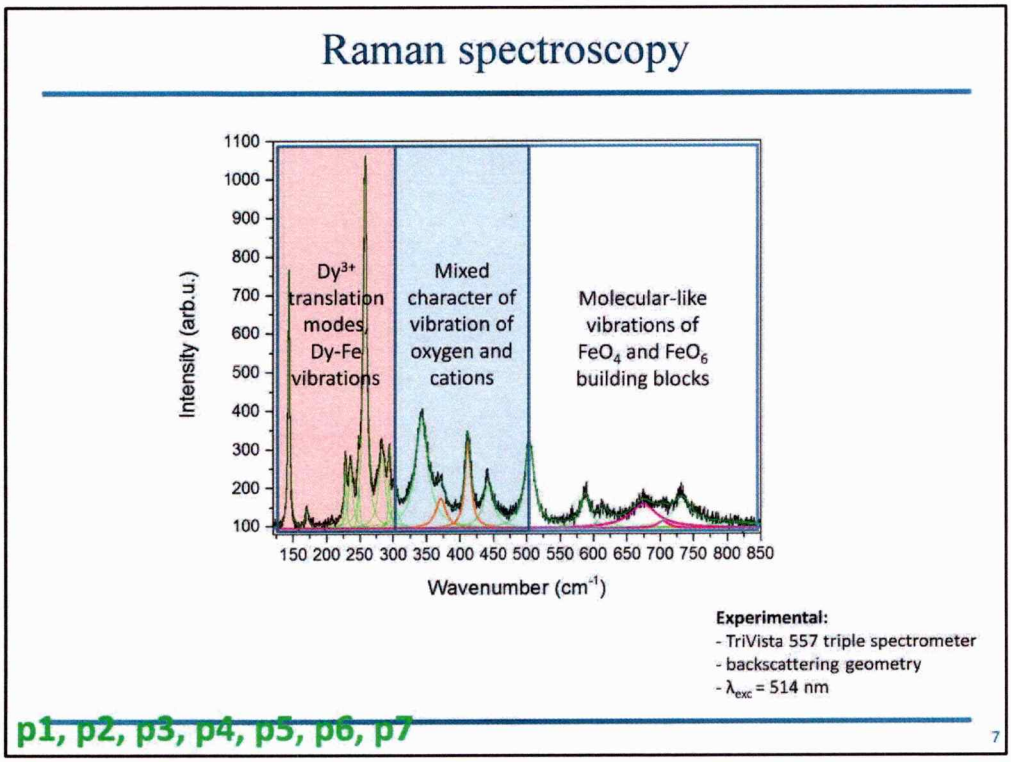
Why it's interesting in nanomaterials:

At the nanoscale, **finite size and surface effects** can enhance or modify the canting, changing magnetic properties.

Spin cycloids can interact strongly with lattice vibrations (**spin–phonon coupling**), making them ideal for studying **magnetoelectric effects** and **novel spintronic applications**.

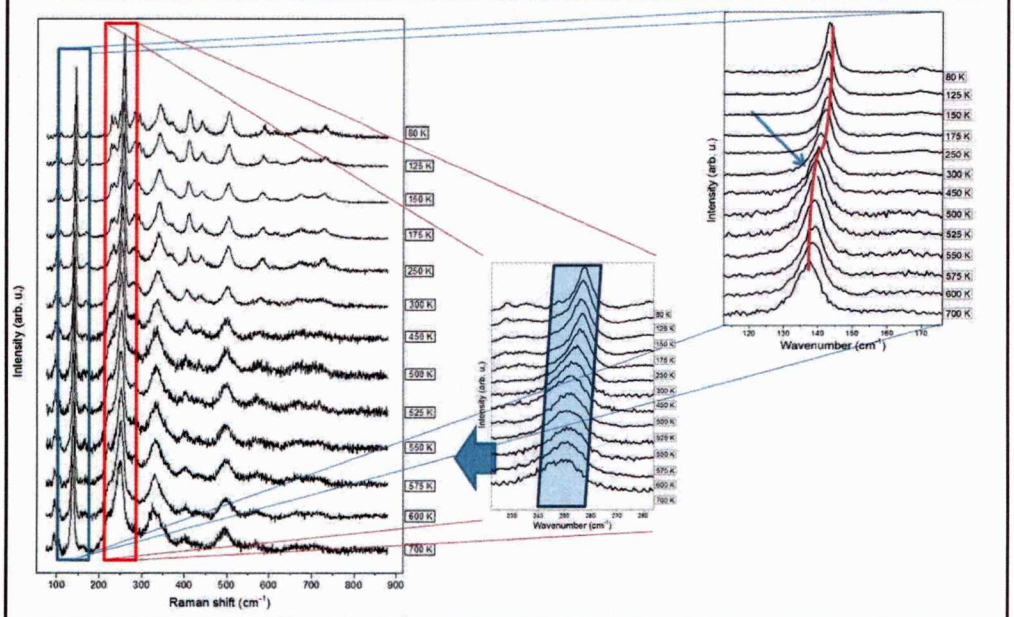
Look at the AFM micrographs in the right side, which show the surface morphology of Tb-doped BiFeO3 thin films at various scales. Notice the high uniformity and well-defined grain structure; as the lead researcher, I used these results to confirm that my synthesis process produces dense and smooth films. This specific morphology is crucial because, at the nanoscale, finite size and surface effects significantly modify the spin canting and magnetic properties. By achieving this level of surface quality, we ensure the strong spin-phonon coupling necessary for novel spintronic aplications.

[6]* slika nije identicna u radu, ali je prica o vezi izmedju kristalne I magnetnih podresetki identicna za Dy i Er gvozdje garnete, sto je na predavanju I istaknuto. Slika ispod, o kompenyacionim temperaturama, nije iz naseg rada, ali je kompenzaciona temperatura I njen znacaj takodje predstavljen u pomenutom radu [6] I veoma je vazan rezultat publikacije koji sam objasnio, diskutovao i oko cega sam diskutovao na kraju predavanja odgovaravsi na pitanja iz publike.



- In this work we investigated the temperature-dependent Raman spectra of Dy3Fe5O12 and BiFeO3 nanomaterials in temperature range from 80K to 700K.
- As for garnets, they have body-centered cubic Oh10 symmetry which, according to factor group analysis, predicts 25 Raman active phonons.
- Less than 25 modes were seen in the experiment due to symmetry breaking and less crystallinity, the mode intensity decreased, and some were not seen in the measurements.
- In literature, whole range is devided in 3 ranges.

Temperature dependent Raman spectra of $Dy_3Fe_5O_{12}$ nanoparticles



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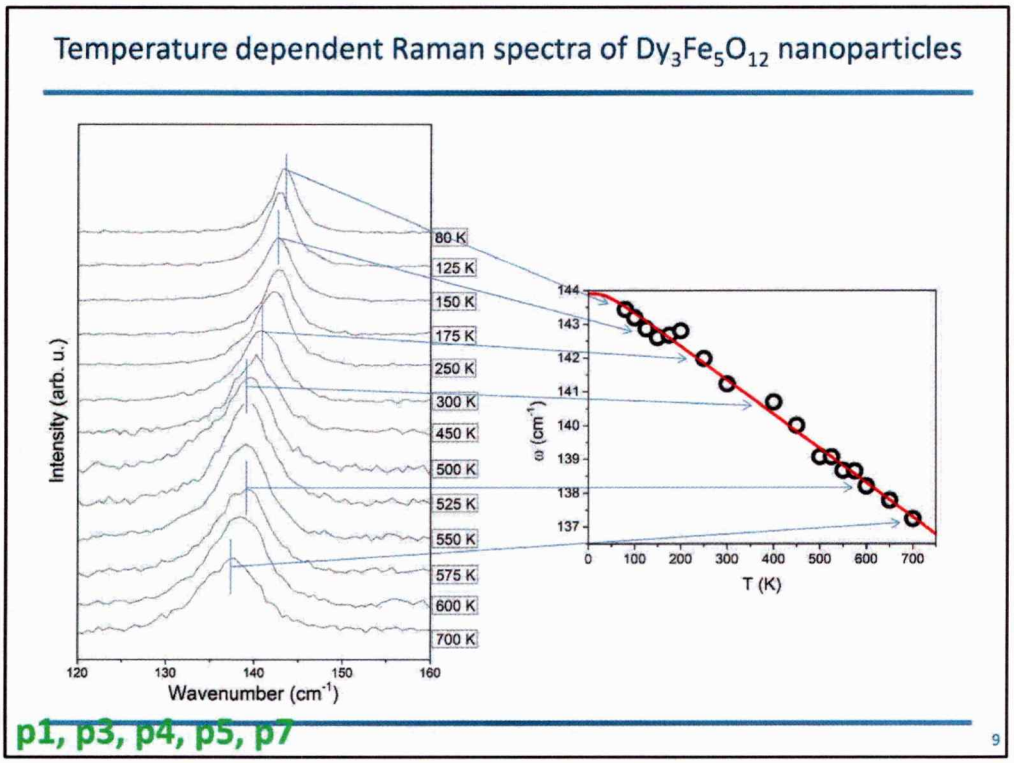


- Red line is anharmonicity.

Frequency shift

Frequency change of a phonon with temperature:

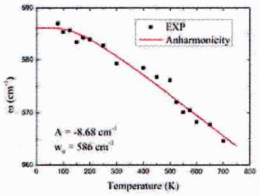
$$\omega(T) - \omega(T_0) = \Delta\omega = \Delta\omega_{latt} + \Delta\omega_{anh} + \Delta\omega_{e-ph} + \Delta\omega_{s-ph}$$

Grüneisen law:

$$\left(\frac{\Delta\omega}{\omega}\right)_{latt} = -\gamma\left(\frac{\Delta V}{V}\right)$$

Anharmonicity:

$$\Delta\omega_{anh} = A\left(1 + \frac{2}{e^{\frac{\hbar\omega(T)}{2k_BT}} - 1}\right)$$



Electron-phonon
- negligible

Spin-phonon:

FM: $H = -2\sum_{i,j} J_{ij}(S_iS_j)$

AFM: $H = 2\sum_{i,j} J_{ij}(S_iS_j)$

$$\Delta\omega = \Delta\omega_{anh} + \Delta\omega_{s-ph}$$

p1, p2, p3, p4, p5, p6, p7

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- First term on the right side is the frequency-independent pure-volume contribution due to the lattice expansion/contraction, explained by Gruneisen law.
- Second term is the anharmonic contribution due to phonon-phonon interaction. This term is the much higher than the first one. First term can be neglected. **In nanostructures, the effect is stronger due to:**
  - **dimensional limitations and**
  - **larger surface area,**

  where bonds are not completely harmonics.
- In semiconductor materials like ferites and garnets, when the carrier concentration is low the third term can be ignored.
- The last term is the spin-phonon contribution, caused by the modulation of the exchange integral by lattice vibration.

Magnetic interaction mechanism

According to Heisenberg model, the magnetic exchange energy in a case of materials with FM and AFM ordering is:

$$H = -2\sum_{i,j} J_{ij}(S_i S_j) + 2\sum_{i,j} K_{ij}(S_i S_k)$$

where S_{ijk} denotes the spin of the *i, j and k*,-nearest and next nearest neighbors magnetic ions.

The frequency shift of a given phonon due to the spin-phonon coupling in materials with competing FM and AFM ordering is given as:

$$\frac{\Delta\omega_{s-ph}}{\omega_0} = -\frac{A\langle S_i S_j\rangle}{S^2} + \frac{B\langle S_i S_k\rangle}{S^2}$$

where *S* is the total spin, *A* and *B* are spin dependent force constants and $\langle S_i S_j\rangle, \langle S_i S_k\rangle$ are spin correlation functions for nn and nnn interactions.

Supposing the same correlation function for $\langle S_i S_j\rangle$ and $\langle S_i S_k\rangle$

$\Delta\omega_{s-ph} \propto \lambda_{s-ph}\langle S_i S_j\rangle$ → dominant *AFM* interaction: $\lambda_{s-ph} > 0$

$\Delta\omega_{s-ph} \propto \lambda_{s-ph}\langle S_i S_j\rangle$ → dominant *FM*interaction: $\lambda_{s-ph} < 0$

From mean-field theory:

$$\frac{\langle S_i S_j\rangle}{S^2} = \left(\frac{M(T)}{M_0}\right)^2 \Rightarrow \Delta\omega_{s-ph} \propto \left(\frac{M(T)}{M_0}\right)^2$$

W. Baltensperger et al. *Helvetica Physica Acta*, 41(1968) 6-7
K. Wakamura et al. *J. Appl. Phys.* 63 (1988) 5824
J.A.Moreira et al. *Phys. Rev. B* 81 (2010) 054447
K. Yosida. *Theory of Magnetism*. Ch 2 (1996) 72-74

p1, p2, p3, p4, p5, p6, p7

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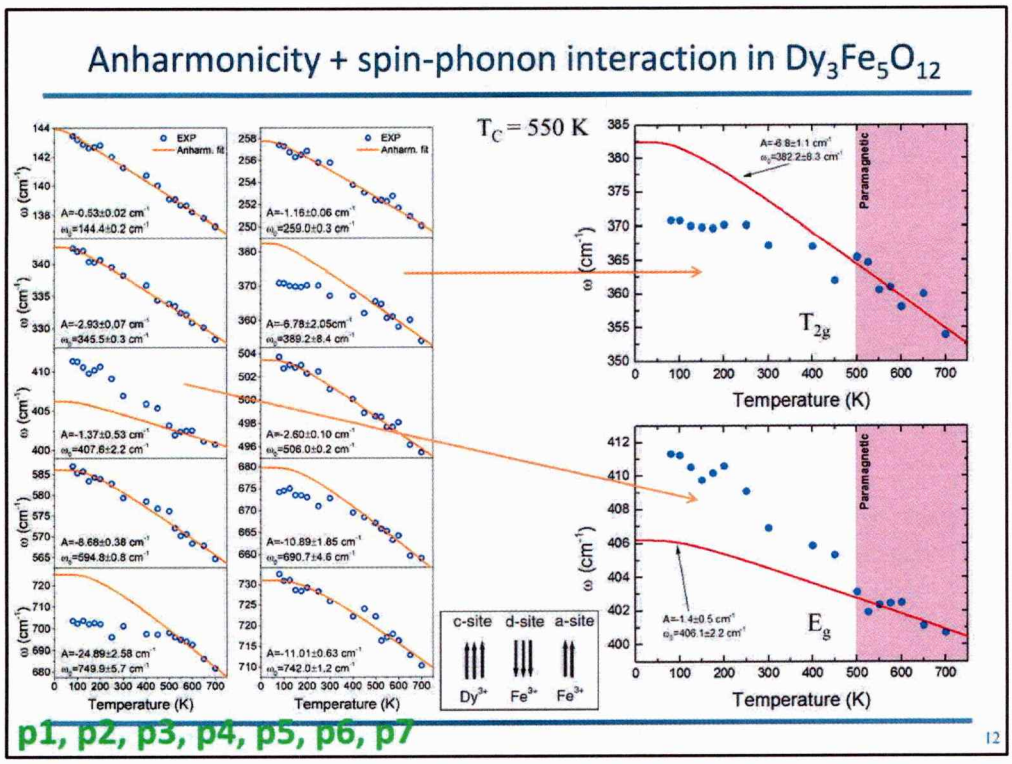
- $\langle S_i S_j\rangle$ показује колико су оријентације спинова на два суседна атома (или јона) међусобно повезане у просеку.

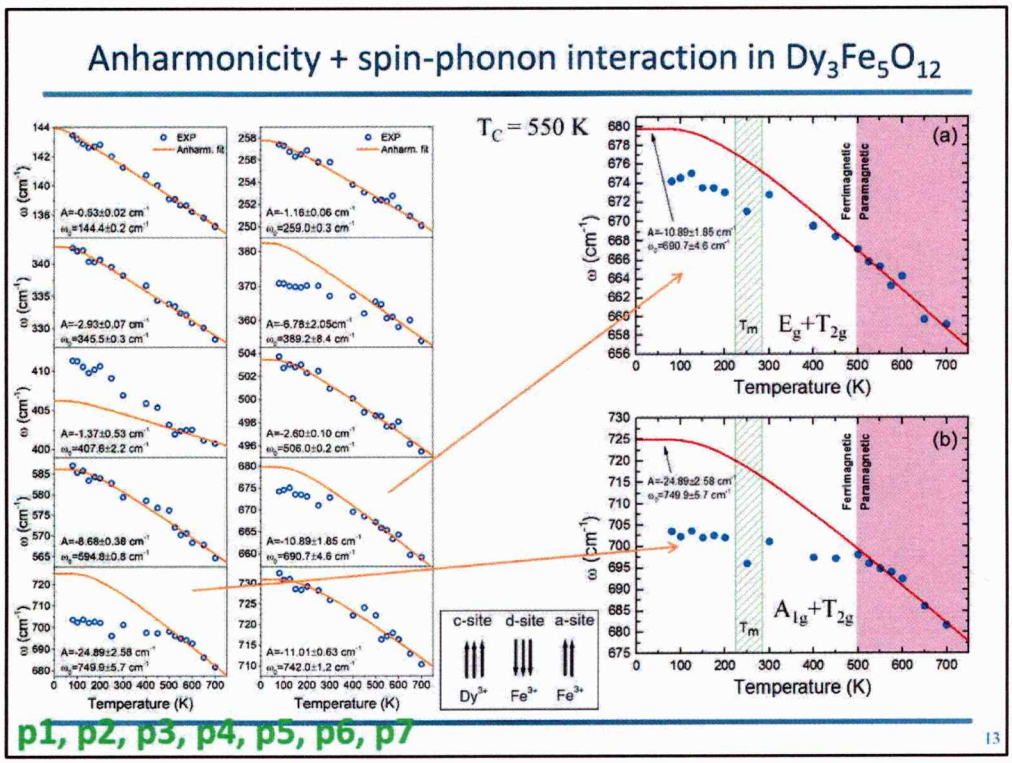
- Ако је $\langle S_i S_j\rangle$ **позитивна**, то значи да спинови теже да буду **паралелни** (што је карактеристично за феромагнетизам).
- Ако је $\langle S_i S_j\rangle$ **негативна**, спинови теже да буду **антипаралелни** (као код антиферомагнетизма).
- Вредност близу **нула** указује на **слабу или никакву корелацију**.
- Овај параметар је кључан у разумевању **магнетног уређења** у материјалима и често се користи у теоријским моделима као што је Хајзенбергов модел.

- M(T) је магнетизација материјала на некој температури T.
- M_0 је магнетизација на апсолутној нули (или на температури када је магнетизација максимална — тј. у потпуно уређеном стању).
- Када поделимо M(T) са M_0, добијамо однос (или релативну вредност) магнетизације.
- Када тај однос узмемо **на квадрат**, то често служи као део модела који описује **спин-фонон спрегу**, **температурну зависност помераја фононских модова** или **декларацију магнетног уређења**.



- The dominant antiferromagnetic superexchange interaction is between Fe spins in tetrahedral and octahedral sites.
- Another important and the second interaction in strength is between Dy and resultant Fe spins in tetrahedral sites. This interaction is antiferromagnetic.
- Mode at 410 cm-1 most corresponds to that type of interaction which is antiferromagnetic, which can be seen in the Raman shift on Figure.

- Compensation temperature is observed in measurements of magnetisation with temperature, where is noticeable drop in magnetisation above 230 K, where Dy sublattice couples antiferromagnetically with the net moment of the Fe^{3+} sublattices, about we discussed in the introduction.
- **Another important thing to notice on these graphs is ferrimegnetic behaviour in phonons which comes from higher frequency range (it means correlated with vibrations of oxygen above Fe ions), where we can apply mean-field theory.**



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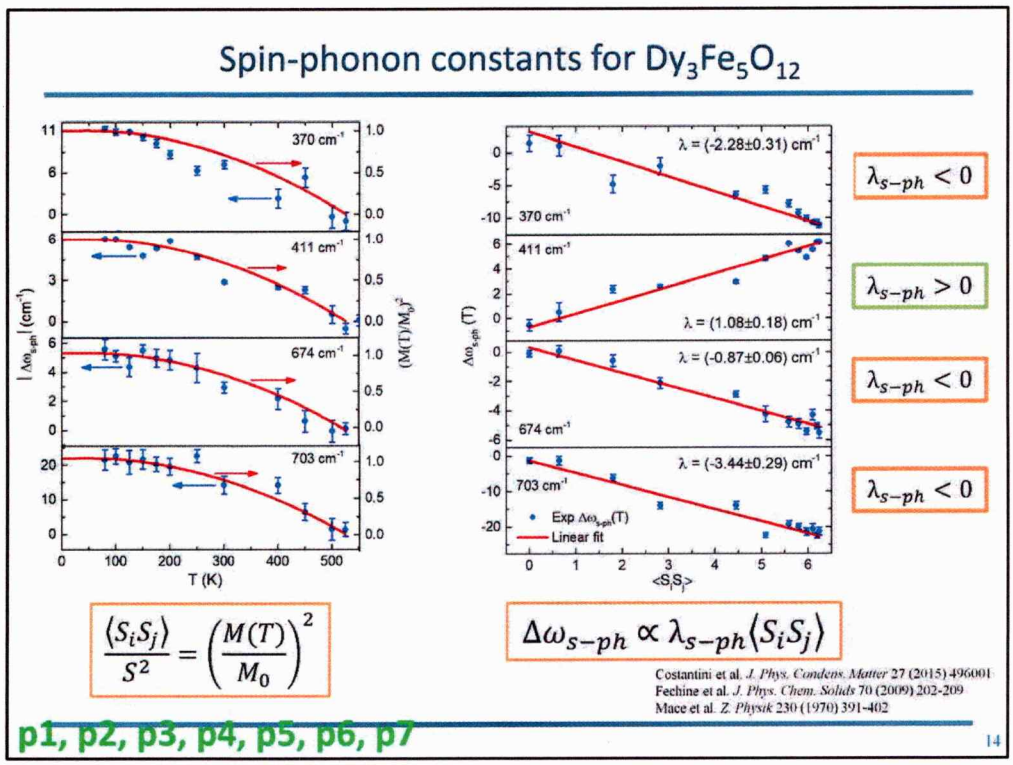
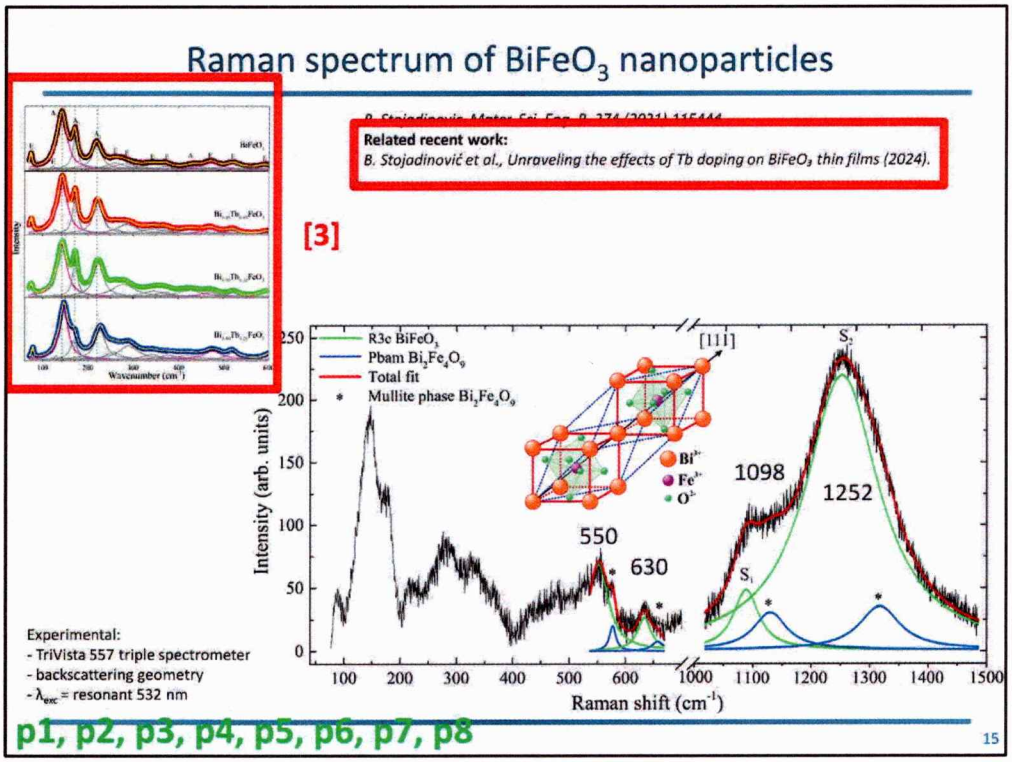


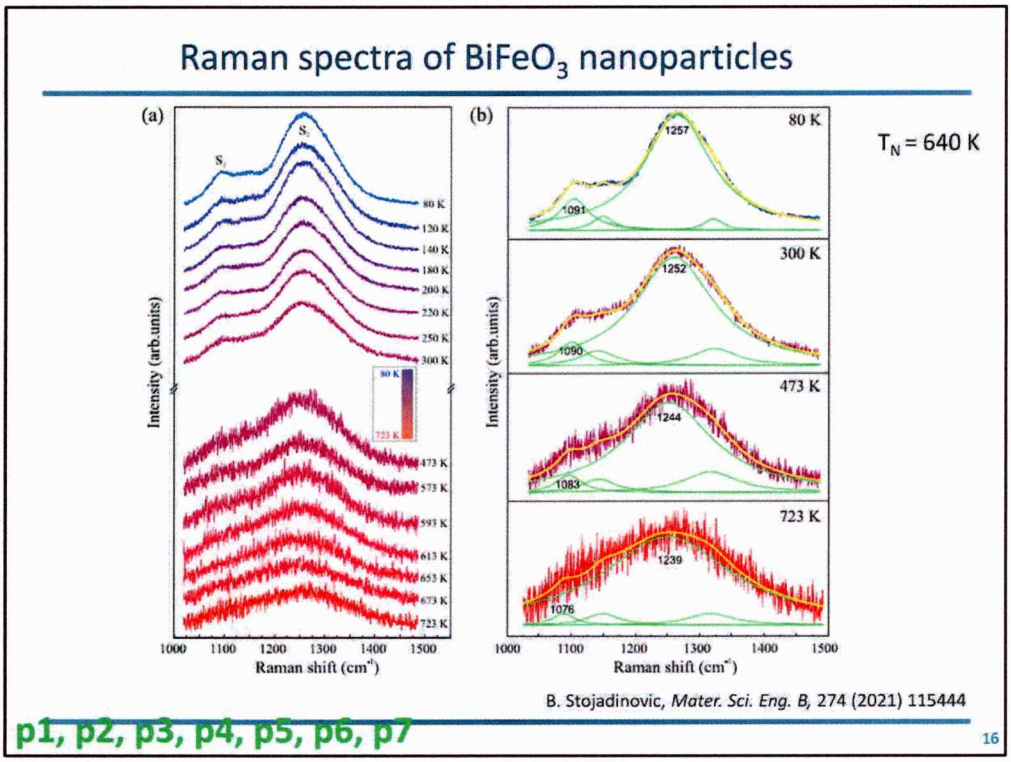
- In order to determine the strength of spin-phonon coupling, it is necessary to separate spin-phonon and anharmonic contributions from the change of the phonon frequency with temperature below Tc.

- These results are related to our recent work on rare-earth iron garnets and their spin-phonon interaction mechanisms.

- From the value for lambda we can conclude that the mode at about 700 cm-1 has 4 times higher spin-phonon constant, thus this mode has a stronger spin-phonon interaction than the mode at about 675 cm-1.

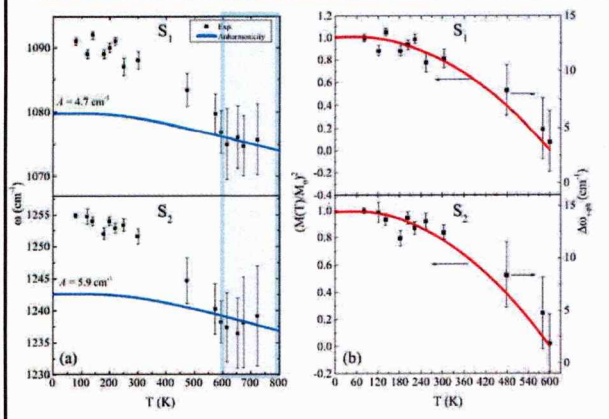


- (prvo prica o materijalu, kratak vec pomenut uvod)
- In the left corner, I am presenting the Raman spectra of Tb-doped BiFeO3 nanoparticles. Notice that the high-frequency modes, primarily responsible for **Fe-O vibrations**, are the most sensitive to doping; the substitution with 4f elements like Terbium induces subtle crystal structure changes that are clearly reflected in the shifting and broadening of these specific Raman bands.
- The high-order Raman modes of the ferroelectric materials are usually very weak, but in the spectrum of BiFeO3 from Fig. 1 an intense multiphonon band is observed.
- The second-order modes S1 and S2, are at the double frequency of the first-order Raman modes.
- The increasing intensity of S1 and S2 modes was attributed to the resonant enhancement when the excitation energy (532 nm ≈2.34 eV) is close to the absorption edge of BiFeO3. The resonant behavior of these modes was explained by exchange mechanism between Fe3+ ions.



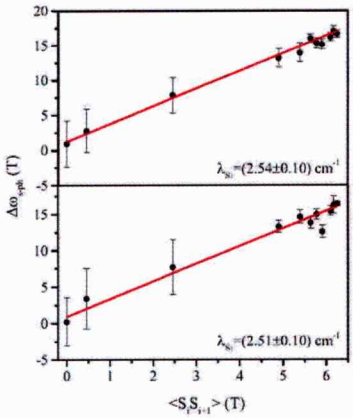
Temperature-dependance of Raman spectra $BiFeO_3$ nanoparticles are shown on Figure left. We can see that the intensity of two-phonon modes S_1 and S_2 decrease and disapear at about temperature of 600K, becaouse of that, as we know that Neal transition temperature is 640K, we corelate this efect to magnetic ordering in this material.

Spin-phonon constants for $BiFeO_3$



$\Delta\omega_{s-ph} \propto \lambda_{s-ph}\langle S_i S_j \rangle$

$\lambda_{s-ph} > 0$



T_N = 640 K

$$\frac{\langle S_i S_j \rangle}{S^2} = \left(\frac{M(T)}{M_0}\right)^2$$

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p1, p2, p3, p4, p5, p6, p7

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- In order to determine the strength of spin-phonon coupling, it is necessary to separate spin-phonon and anharmonic contributions from the change of the phonon frequency with temperature below Tc.

- **Within the mean-field theory, spin-spin correlation function Si·Si+1 is proportional to the square of normalized magnetization.**
- The (M(T)/M0)2 curve was obtained using a numerical solution for Briluen function in a case of Fe3+ ions having spin S=5/2.
- Obviously, Δωs−ph(T) scales very good with (M(T)/M0)2 curve confirming that the significant deviation of two-phonon frequencies from anharmonic behavior below Tn is actually due to spin-phonon interaction.

- According to Eq., from the plots Δωs−ph(T) vs Si · Si+1(T), we applied lineary fit for this graphs, where the spin-phonon coupling constant λ can be determined for both phonon modes. We can see that spin-phonon coupling constant λ for both modes are same, meaning that spin-phonon interaction is the same for both.

Conclusions

- Significant deviation of certain phonon frequencies from anharmonic behavior below T_C are seen in $Dy_3Fe_5O_{12}$. Such behaviour is characteristic for spin-phonon coupling in materials with dominant FM ordering.

- In a case of $BiFeO_3$ two-phonon frequency deviation below T_N was ascribed to spin-phonon coupling in materials with dominant AFM ordering.

- The spin-phonon interaction in both materials is successfully described by mean field theory.

- These results represent part of the research published by the author in the last years.

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Recent publications of the author (2024–2025):

1. Amjed Abdullah Karkad, Andrea Pirković, Milena Milošević, Bojan Stojadinović, Katarina Šavikin, Aleksandar Marinković, Aleksandra A. Jovanović, "Silibinin-Loaded Liposomes: The Influence of Modifications on Physicochemical Characteristics, Stability, and Bioactivity Associated with Dermal Application", Pharmaceutics, 16 (2024) 1476. **M21a**
2. Mirjana Mićević, Sonja Čalija, Lela Korićanac, Jelena Žakula, Aleksandra Vilotić, Marko Radović, Igor Golić, Aleksandra Korać, Mirjana Nacka-Aleksić, Bojan Stojadinović, Zorana Dohčević-Mitrović, "Probing the effects of dextran-coated CeO_2 nanoparticles on lung fibroblasts using multivariate single-cell Raman spectroscopy", Nanotoxicology, 19 (2025) 100-118. **M21a**
3. Bojan Stojadinović, Igor Popov, Borislav Vasić, Dejan Pjević, Milena Rosić, Nenad Tadić, Zorana Dohčević-Mitrović, „Unraveling the effects of terbium doping on the electronic structure and conductivity of $BiFeO_3$ thin films", Applied Surface Science, 710 (2025) 163753. **M21a+**
4. Jelena Bobić, Nikola Ilić, Robertas Grigalaitis, Aleksandar Radojković, Mirjana Vijatović Petrović, Saso Gyergyek, Ivan Stijepović, Bojan Stojadinović, Adis Dzunuzović, Algimantas Kežionis, Tomas Šalkus, Juras Banys, "Effect of gadolinium substitution on layer-structured Aurivillius $Bi_5Ti_3FeO_{15}$ ceramics", Journal of Rare Earths, In Press. **M21**,
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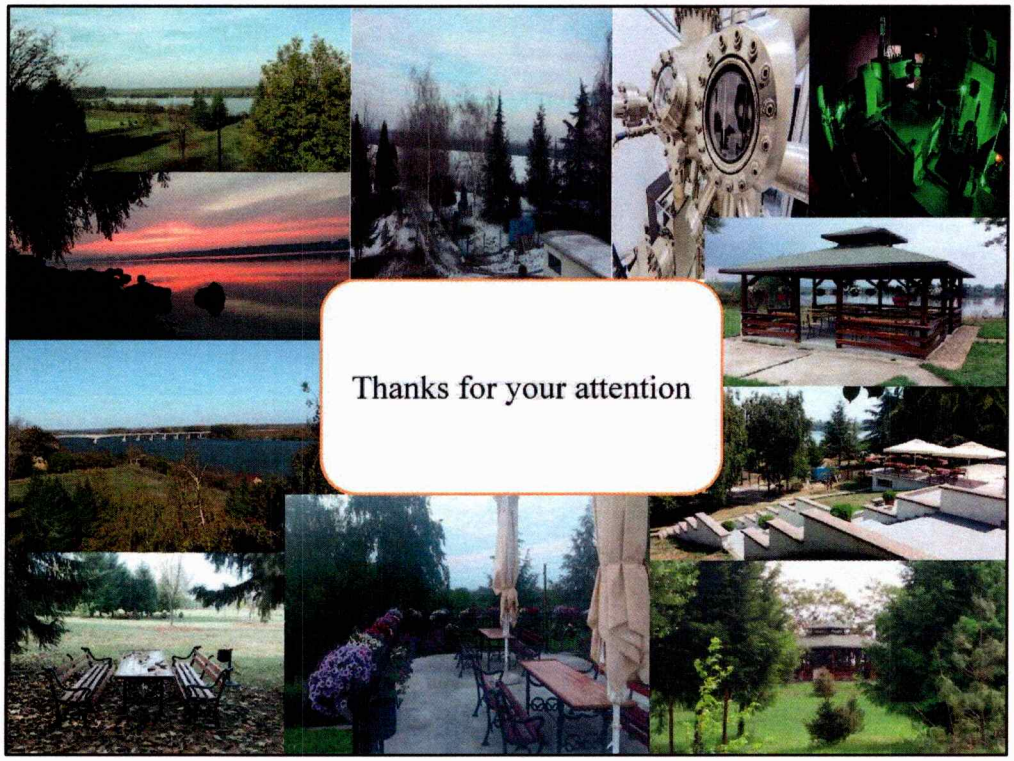
Thanks for your attention