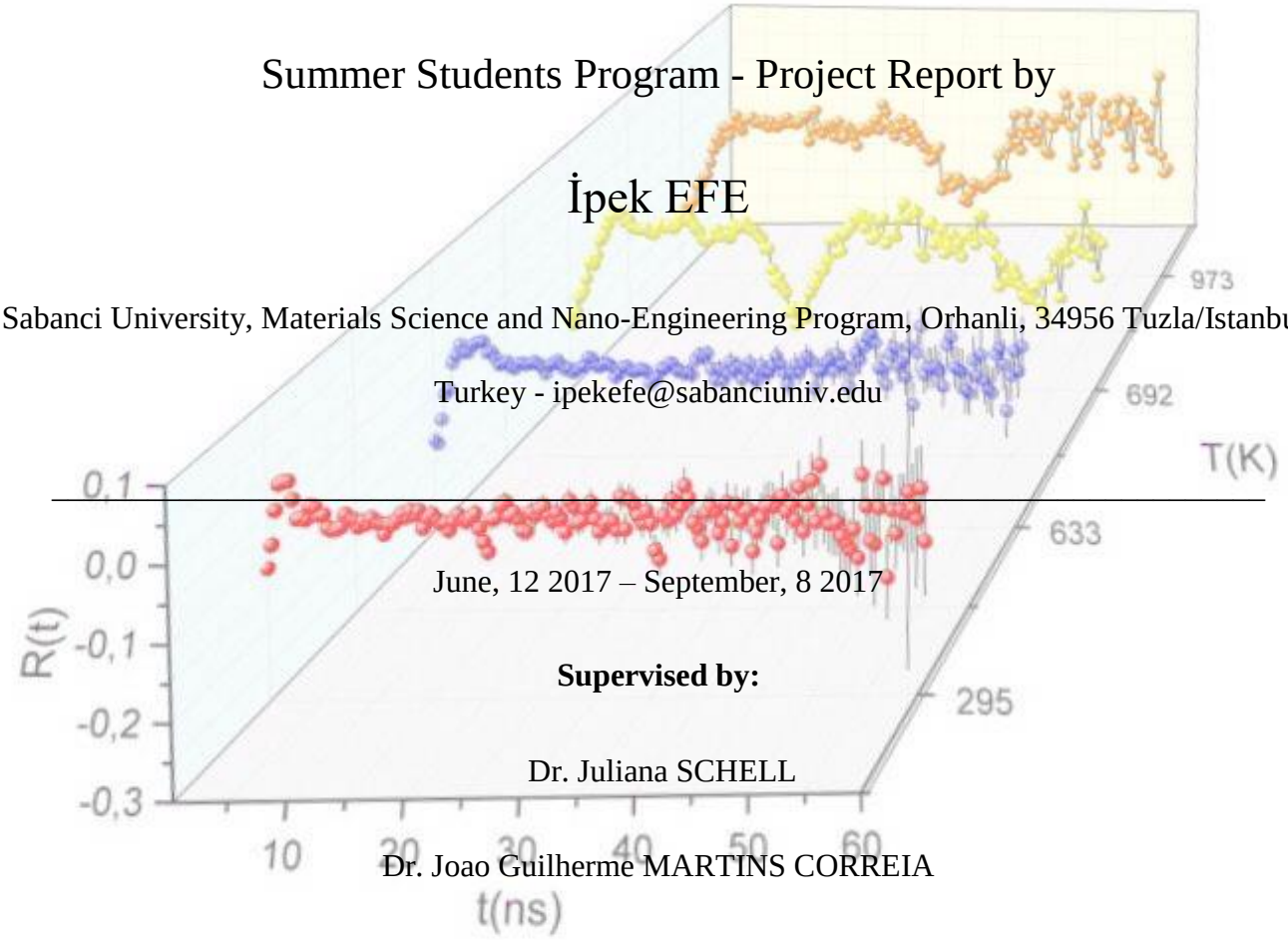
Investigation of electromagnetic properties of $BiFeO_3$ by Time Differential Perturbed Angular Correlation (TDPAC) technique at ISOLDE

Summer Students Program - Project Report by

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Abstract

Time differential perturbed angular correlation (TDPAC) technique is one of the most sensitive techniques to study about the electric and magnetic fields at the individual lattice points. It benefits from the hyperfine interactions between the probe atom and its neighborhood. Multiferroic materials have been intensively studied to promote and understand the possibility of controlling magnetic properties by electric fields instead of magnetic fields which opens the path to faster, smaller, and more energy-efficient spintronic devices, such as memory elements, high-frequency magnetic devices, and micro-electro-mechanical systems, for data-storage technologies. $BiFeO_3$ is one of the famous and important multiferroic materials since it shows both antiferromagnetic and ferroelectric behavior at room temperature. In this study, we report on the first time-differential perturbed angular correlation (TDPAC) measurements carried out on polycrystalline $BiFeO_3$ samples using the nuclear probe 181Hf(181Ta) after implantation at the Bonn Radioisotope Separator (BONIS). The measurements have been done at a very broad temperature range from 296 K to 973 K and we have found the temperature dependent behaviors of the hyperfine interaction parameters and clearly observed the effects of the transition from anti-ferromagnetic to paramagnetic structure at Néel temperature. Two different lattice sites have been observed and these can be assigned to an undisturbed Fe-site and Fe-site with O vacancies in the lattice.

1. Introduction

Time differential perturbed angular correlation (TDPAC) technique is one of the techniques which benefits from the hyperfine interactions between the probe atom and its neighborhood. TDPAC is a very sensitive method used to study the local electric- magnetic fields in the lattice. TDPAC method uses radioactive nuclei which decay by emitting γ-γ rays and have a half-life long enough to investigate the decays within the time resolution of the machine as a probe atom. In our experiment, we used ^{181}Hf(^{181}Ta) as the probe atom. Our aim is to understand the temperature dependent multiferroic behavior of Bismuth Ferrite ($BiFeO_3$) compound. Since radioactive ^{181}Hf decays in 2 steps and emits 2 γ rays, these γ rays' directions are angularly correlated and the angular distribution of these photons depends on the spin of the nuclei. In solids, the nuclear moments of the intermediate state interact with the hyperfine field causing a time dependent redistribution of the population of the m-substates, which perturbs the angular distribution of the second γ_2-quantum [4]. TDPAC detectors detect these γ rays emitted from the probe atom as a function of time. The angular correlation function W(θ) that gives the ratio of the likelihood of detecting a photon at an angle θ to the likelihood of detecting a photon at an angle of 90° is given by [6]

$$W(\theta) = 1 + A_{22}P_2(\cos(\theta)) + A_{44}P_4(\cos(\theta)) \qquad (1)$$

where $A_{22} = 0.1020$, $A_{44} = 0.0091$ are the anisotropy coefficients of the γ-γ cascade and P_n represent the Legendre polynomials. And the number of coincidences measured by the apparatus can be calculated as

$$N(\theta,t) = N_0\, e^{-\lambda t} \cdot W(\theta) \qquad (2)$$

where N_0 is the total counting rate, λ the decay constant [2]. The perturbation function R(t) can be calculated as

$$\mathrm{R(t)} = 2.\frac{N(180°,t) - N(90°,t)}{N(180°,t) + 2N(90°,t)} \qquad (3)$$

If there are probe atoms exposed to *j* different lattice environments, and each of them creates a characteristic field gradient at fraction *f* of probe atom sites, the perturbation function becomes

$$\mathrm{R(t)} = A_{22} \sum_{\mathrm{j}} f_{\mathrm{j}} G_{22}^{j}(\mathrm{t}) \qquad (4)$$

If the decay is not perturbed by external magnetic or electric fields, then the ratio R(t) is constant in time and equal to the coefficient A_{22}. A perturbation in the spectra can be resulted from either

magnetic or electric hyperfine interactions. The electric hyperfine interactions occur between the nuclear electric quadrupole moment Q of the probe nucleus and the external Electric Field Gradient (EFG) caused by its neighborhood. The asymmetry parameter $\eta = |(V_{xx} - V_{yy})|/|V_{ZZ}|$ characterizes the EFG tensor asymmetry and the major component of the EFG tensor (V_{zz}) can be obtained by the observable spin dependent quadrupole frequency ω_Q, expressed as:

$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar} \quad (5)$$

where I is the nuclear spin and Q the nuclear quadrupole moment. On the other hand, the magnetic hyperfine interactions occur between the magnetic dipole moment of the nucleus and the magnetic field around it. Similarly, the Larmor frequency $\omega_L = -g\mu_N B/\hbar$ gives the precession frequency of the nuclear spin around the axis of the magnetic hyperfine field B, where g denotes the g-factor of the intermediate state and μ_N the nuclear magneton. In addition, β is the Euler angle between the V_{zz} and the B.

By studying the perturbations in the angular correlation between the γ rays with the changing temperature, the temperature dependent electromagnetic properties of the individual lattice sites can be understood and the behavior of the material around its critical temperatures can be studied.

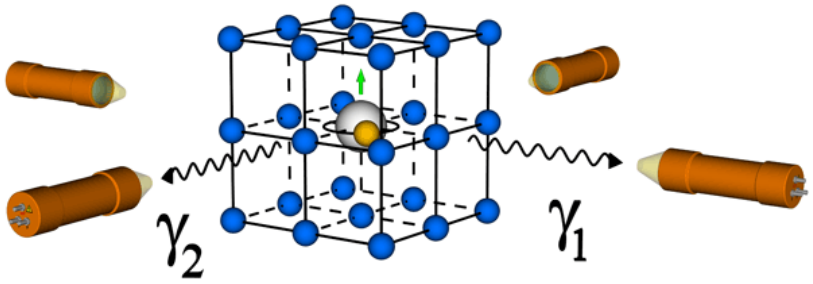
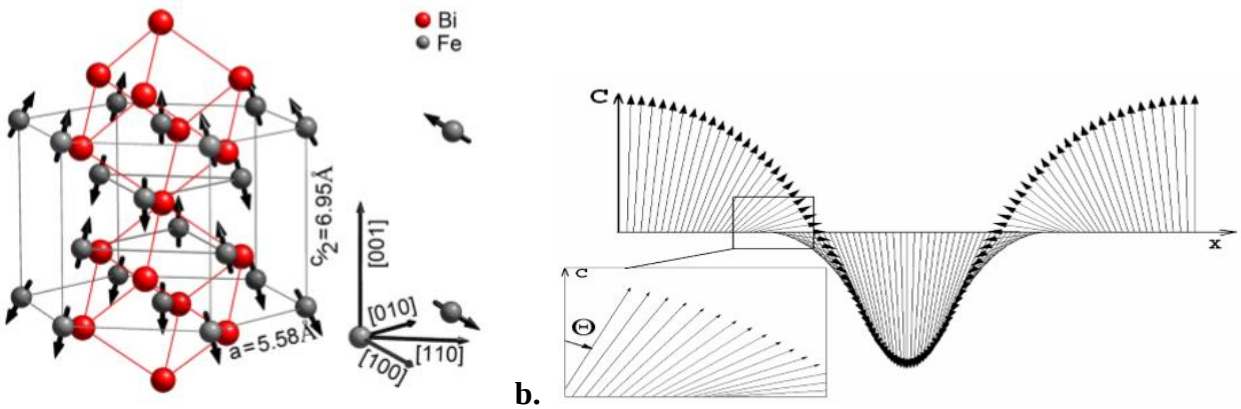


Figure 1. Scheme of a 4-detector TDPAC machine [10]

The materials that exhibit more than one of the ferroelectricity, ferromagnetism or ferroelasticity simultaneously are called multiferroics. The ones that exhibit ferroelectricity and ferromagnetism are called magnetoelectric materials and their ferroelectric and ferromagnetic properties are coupled which means it is possible to create a magnetization by applying an electric field; and electric polarization by a magnetic field. Multiferroics have become increasingly important due to their enormous potential for development of the magnetoelectric devices, spintronic devices and more efficient data storage technologies. Bismuth ferrite ($BiFeO_3$) is one of the most famous multiferroics. It exhibits

antiferromagnetic ordering below its Néel temperature (T_N ~653 K) and paramagnetic above T_N together with ferroelectric ordering (T_c ~1103 K). It has rhombohedrally-distorted perovskite structure (Figure 2.a) like most of the other multiferroics. But it has a unique place since it exhibits both antiferromagnetic and ferroelectric behavior at room temperature and it is found that the magnetic moments of Fe^{3+} cations have been ordered in a unique way called (anharmonic) cycloidal structure along the $[110]_{hex}$ vector (Figure 2.b) in the lattice. Spin cycloid makes $BiFeO_3$ more significant as controlling this behavior can open new pathways for magnetoelectric memory and spin-wave-based logic gates [1]. Apart from all these unique properties, bismuth ferrite is thought to have many more properties that have not been revealed yet. In this project, we aimed to investigate the temperature dependence of the hyperfine parameters on $BiFeO_3$. During my summer internship, I have analyzed the data we have obtained from TDPAC measurements and have joined the Cd beam-time in week 33 and taken active part in the experiments and data acquisition. The results I have obtained is presented in the Results & Discussion section.



a. **b.**

Figure 2. a) Rhombohedrally-distorted perovskite structure of $BiFeO_3$ [5]; **b)** Spin cycloid structure of the Fe^{3+} cations along the $[110]_{hex}$ vector [11].

2. Experimental Method

First step for this is having the ^{181}Hf atoms implanted into the BFO lattice. This has been done at the Bonn Radioisotope Separator (BONIS), in Germany. The samples were shipped to ISOLDE-CERN for this study. Following the implantation, radiation damage was annealed in air up to temperatures of 700 °C in three steps. Firstly, at 500 °C for 24 h, followed by 600 °C for 9 hours and 700 °C for 10 hours. The TDPAC measurements were carried out at ISOLDE-CERN [12] using a digital set up [9] with six conical $LaBr_3$: Ce detectors scintillators with a time resolution of 0.7 ns (FWHM). The measurement at

each temperature lasted several hours. The thermal treatment at 500 °C, 600 °C and 700 °C were performed during the measurements. The theoretical perturbation function was fitted to the spectra using the Nightmare [7] software to extract the hyperfine parameters [8].

3. Data Analysis

I have used the software Interlude [3] to find time zeros for all the spectrums obtained by 30 detector-combinations for the measurements at each temperature. After finding the time zeros I have used the software Nightmare [7] to find the hyperfine parameters for $BiFeO_3$ samples measured at different temperatures by obtaining the best fitting. I have analyzed the data from 14 measurements each at a different temperature between 23 °C and 700 °C.

4. Results & Discussion

The fitting results are shown in the Figure 3 at different temperatures.

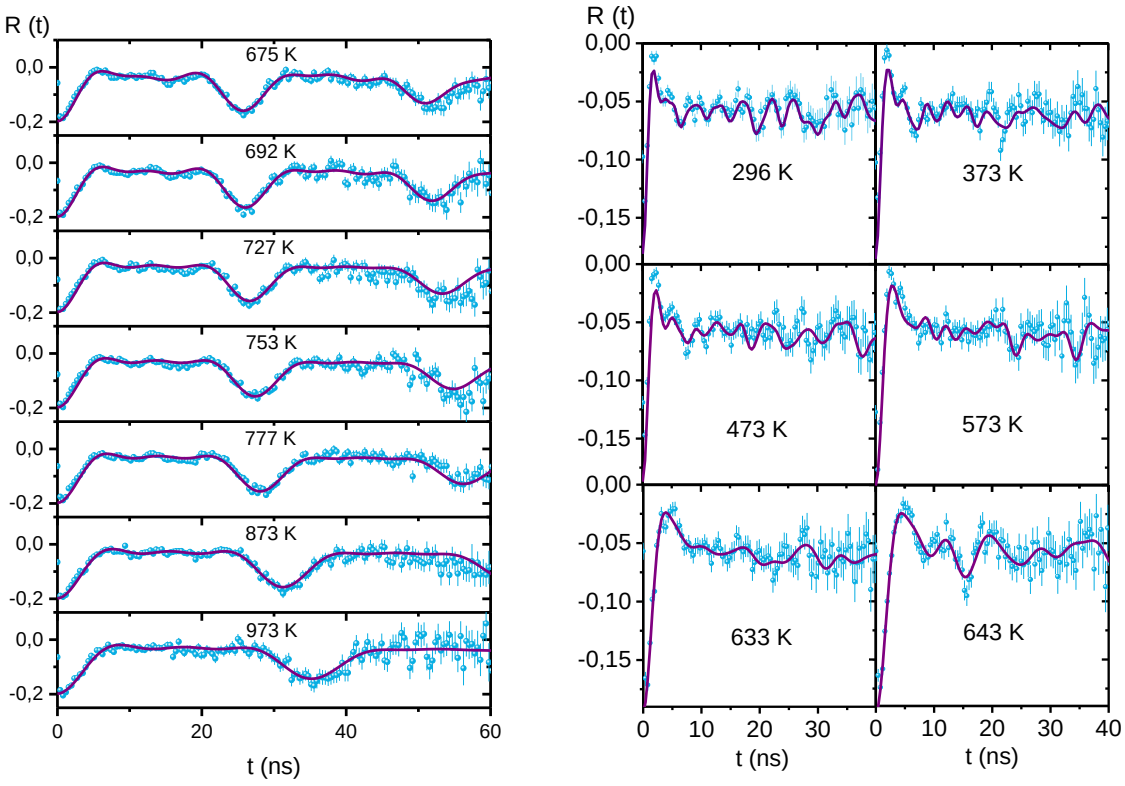


Figure 3. TDPAC spectra measured at several temperatures. Least-square fittings have done by software Nightmare for the measurements at different temperatures.

Apparently, the 2 different data sets contributing to the fitting have been observed and this indicates the hyperfine interactions from 2 different atomic sites in the $BiFeO_3$ lattice. After the least-square fittings were made, the hyperfine parameters for each temperature have been found and presented in Figure 4. The calculated parameters are quadrupole frequency, ω_Q, which carries information about the electric hyperfine interaction; asymmetry parameter, η, which represents the asymmetry in the EFG tensor as explained above; damping (δ), which shows the EFG distribution at the lattice sites; fraction (f), which shows the fraction of the different sites and Larmor frequency, ω_L, which carries the information about the magnetic hyperfine interactions.

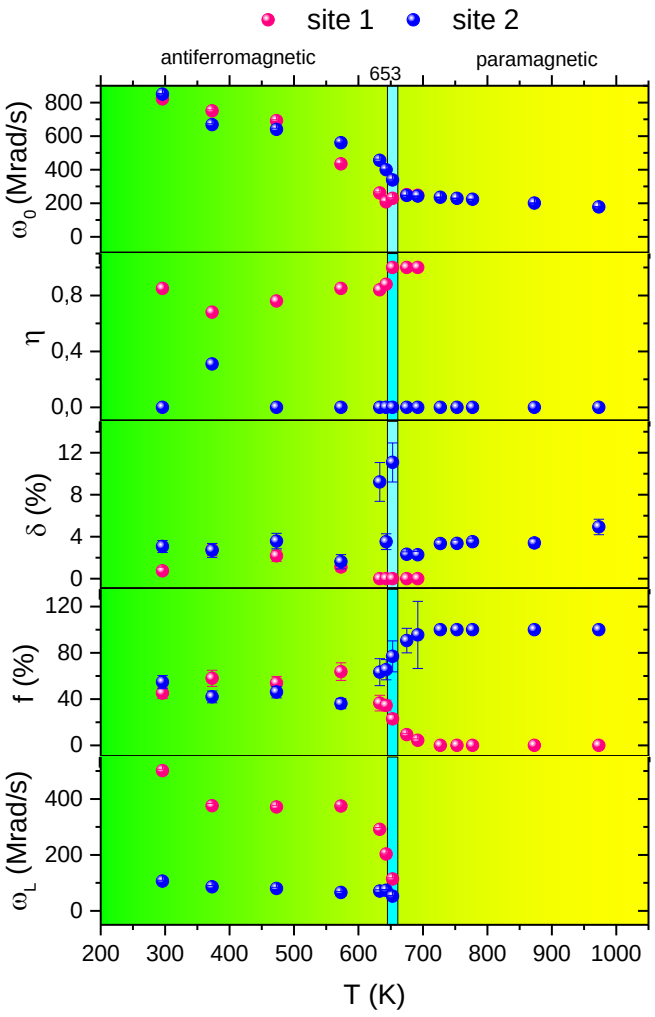


Figure 4. Experimental hyperfine parameters with changing temperature.

For the discussion, since the Néel temperature (T_N =653 K) is a critical temperature and the transition point for $BiFeO_3$ from antiferromagnetic to paramagnetic behavior, the results can be examined in 3 different regions: below T_N, around T_N and above T_N.

Firstly, it can be observed that site-2 is not contributing to the data above 692 K, meaning that the site-2 environment disappears at elevated temperatures. The quadrupole frequency values calculated from the fittings for the sites are close to the simulated values for the Fe-site, with and without oxygen vacancies near to the ^{181}Hf(^{181}Ta) atoms. It has been observed that below T_N the quadrupole frequency has decreased with increasing temperature for both sites and dropped suddenly around T_N. The non-linear decrease resulted from the thermal expansion of the lattice was also influenced by the non-symmetrical magnetic hyperfine interactions and the O vacancies around the probe atom and the sudden decrease at T_N indicates a transition that has changed the lattice environment. Above T_N, since the magnetic hyperfine interactions have disappeared and the defects have been removed due to the treatment at elevated temperatures in the air environment. Thus, the decrease has become linear and has been assigned to the decreasing electric field due to the thermal expansion of the lattice. The asymmetry parameter is zero for site-2 and has higher values for site-1. The zero-asymmetry parameter indicates the symmetrical and unperturbed lattice environment that is resulted from absence of defects around the probe atom. On the other hand, the high asymmetry parameter for the site-1 indicates a distorted lattice geometry by the defects, in this case the O vacancies. The distribution of EFG increases suddenly at T_N, which indicates the extreme attenuation of the quadrupole interaction and the magnetic precession pattern which points a transition at T_N and this can be seen in Figure 5. While the fractions of the both sides are close to equal below T_N; the fraction of site-2 starts increasing around T_N and it dominates the site-1 above T_N, indicating the site-1 environment is gradually disappearing with the increasing temperature. This behavior also indicates that site-1 is an environment with defects and for our case, it most likely is the environment with O vacancies. Lastly, below T_N, Larmor frequency for both sites are decreasing by increasing temperature. While the decrease for site-2 is low, the decrease for site-1 is higher. This is similarly caused by the less stable structure of the environment with defects. Above T_N, the Larmor frequency disappears since $BiFeO_3$ has been changed to paramagnetic from anti-ferromagnetic; thus the spontaneous magnetization creating the magnetic field around the probe nuclei has disappeared.

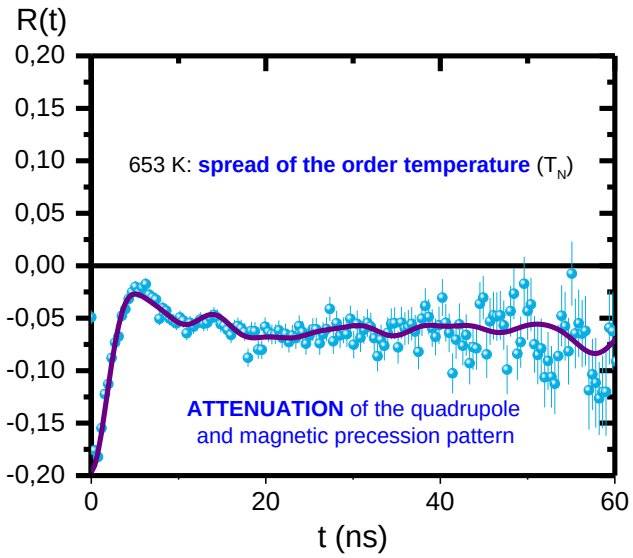


Figure 5. TDPAC spectrum and its fitting at the Néel temperature (650 K) indicating extreme attenuation of the precession pattern.

5. Conclusion

As a conclusion, we have carried out the first TDPAC measurements for $BiFeO_3$ at a very broad temperature range from 296 K to 973 K and found the temperature dependent behaviors of the hyperfine interaction parameters. We have clearly observed the effects of the transition from anti-ferromagnetic to paramagnetic structure at Néel temperature. We have observed two different lattice sites that can be assigned to an undisturbed Fe-site and Fe-site with O vacancies.

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APPENDIXES

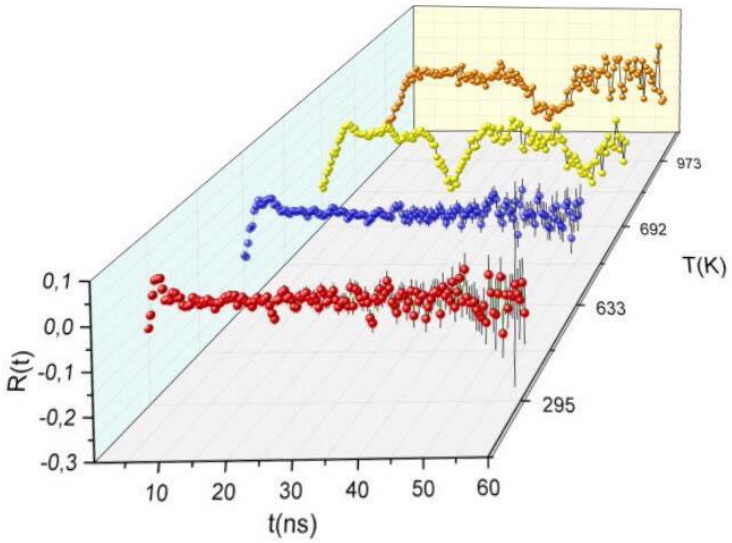


Figure 1. Temperature dependent behavior of perturbation spectra in a 3D manner.