JOINT INSTITUTE FOR NUCLEAR RESEARCH
Frank Laboratory of Neutron Physics

FINAL REPORT ON THE START PROGRAMME

Procedure for refinement of neutron diffraction patterns

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Abstract

In this work we will focus in the procedure of processing data of neutron diffraction. We will use doped spinel ferrite $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ as an example and calculated structural and magnetic properties. Starting from the time-of-flight neutron diffraction data, Rietveld analysis was performed and were obtained parameters like lattice constants, atomic coordinates, interatomic distances and angles and magnetic moments. The diffraction patterns were recorded in the 24 ºC to 151 ºC range of temperature and 0.8 GPa to 4.7 GPa range of pressures. By increasing the temperature and the pressure, a gradual suppression of the magnetic moments of iron ions in both crystallographic sites was observed. This effect corresponds to a magnetic phase transition from the ferrimagnetic state to paramagnetic one. The lattice parameters, interatomic bond lengths and angles, magnetic moments of iron ions as functions of temperature and pressure were obtained.

Introduction

The spinel-type ferrites are an important class of magnetic materials due to their technological applications [1, 2]. In particular, canted antiferromagnetic, ferrimagnetic, spin glass and semi-spin glass states can be realized in these compounds [3]. A significant saturation magnetization, relatively high electrical resistivity, low electrical losses and a good chemical stability [4, 5] make these materials important for broad range of technological applications as transformer cores, radio frequency circuits, rod antennas, data storage devices, magnetoelectronics, etc. [6, 7].

The diversity of the magnetic properties of spinel ferrites is caused by the peculiar distribution of iron ions between two crystallographic A and B sites with tetrahedral and octahedral oxygen coordination in the cubic spinel crystal structure [8]. The general chemical formula of a ferrite is AFe_2O_4, where A is a divalent element. The cubic ferrites have the spinel crystal structure of the type $MgAl_2O_4$. In the normal spinel arrangement, the A^{2+} cations occupy only tetrahedral sites, while the Fe^{3+} cations occupy only octahedral sites. In the inverse spinel arrangement, the tetrahedral sites are occupied by the Fe^{3+} cations, while the octahedral sites are occupied half by the A^{2+} cations and half by the Fe^{3+} cations [6].

Neutron diffraction is a powerful technique that provides information about both the crystal structure and the magnetic properties of matter. Research at high pressures is the only direct method for controlled changes in physical properties due to variations in interatomic distances and valance angles. Such research provides a unique opportunity to study the structural aspect of the formation of the physical properties of compounds, including magnetic ones.

The staff of the Frank Laboratory of Neutron Physics of JINR (Dubna, Russia) has more than twenty years of experience in developing high-pressure neutron scattering methods. In recent years, a new high-luminosity diffractometer DN-6 has been developed, combining a higher incident neutron flux and a wide aperture of the detector system. The DN-6 diffractometer includes a neutron beam chopper in phase with the reactor pulse, a curved neutron guide based on supermirrors with a parabolic focusing section to ensure a high neutron flux on the sample and a detector system with a large solid angle that allows to carry out neutron diffraction experiments with extremely small volumes (about 0.01 mm^3) of samples under research. High pressure chambers with sapphire and diamond anvils are used on a specialized neutron diffractometer DN-6 to study microsamples. The available pressure range extends up to 50 GPa.

Diffractometer experiments are carried out in axial geometry, when an incident collimated neutron beam passes through a sapphire single crystal

anvil and scatters on the sample. Scattered neutrons are registered separately using each of the detector ring counters. To obtain low temperatures, a closed cycle helium refrigerator is used. The high pressure chamber is loaded into a cryostat that allows to carry out further research on the structures and magnetic phase diagrams of a wide range of objects at various temperatures and pressures.
In the present work, Rietveld analysis based on structure refinement has been adopted for compound $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ to determine several parameters: lattice constants, atomic coordinates, interatomic distances and angles and magnetic moments. The structural and magnetic properties of doped ferrite have been studied through implementing the method of neutron diffraction at high pressures up to 4.7 GPa and in temperature range 24 ºC to 151 ºC. FullProf and Diamond softwares were utilized for refinement and interatomic distances and angles measurement. The primary aim for the study is to acquire the knowledge regarding data processing, work methodology and to analyse the results.

Experimental method

The starting materials, Fe_2O_3, ZnO, CuO and Ga_2O_3 (with purity 99.99%), were used to synthesize a powder sample of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ ferrite through solid-state reactions. The mixture of the oxide powders was annealed at 1100 ºC within 72 h. The obtained material was milled and annealed again at the same temperature conditions to improve homogeneity. The final powders were pressed into pellets and sintered at 1200 ºC for 8h. Neutron powder diffraction measurements at ambient and high pressures up to 4.7 GPa were performed at ambient temperatures with the DN-6 diffractometer at the IBR-2 high-flux pulsed reactor (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia) using the sapphire anvil high-pressure cell. Several tiny ruby chips were placed at different points on the sample surface and the pressure was determined by a standard ruby fluorescence technique. Diffraction patterns were collected at scattering angle $2\theta = 90^o$ with the resolution $\Delta d/d = 0.012$ at $d = 2$ Å. In addition, the sample $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ was heated up to 151 ºC by means of special heater [7]. The temperature was measured by the K-type thermocouple. The Neutron powder diffraction data were analyzed by the Rietveld method using the FullProf software.

Results and Discussion

1. Temperature dependence measurements

Experimental points and calculated profiles by the Rietveld method of neutron diffraction patterns of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ measured at different temperatures are shown in Fig. 1. A temperature dependence of lattice parameter of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ spinel is shown in Fig. 2. We can observe that at high temperatures the lattice parameter will increase. Due to the cubic structure, the unit cell volume will have similar behaviour for the lattice parameter. Hence, as the temperature increases the ferrite volume will increase.

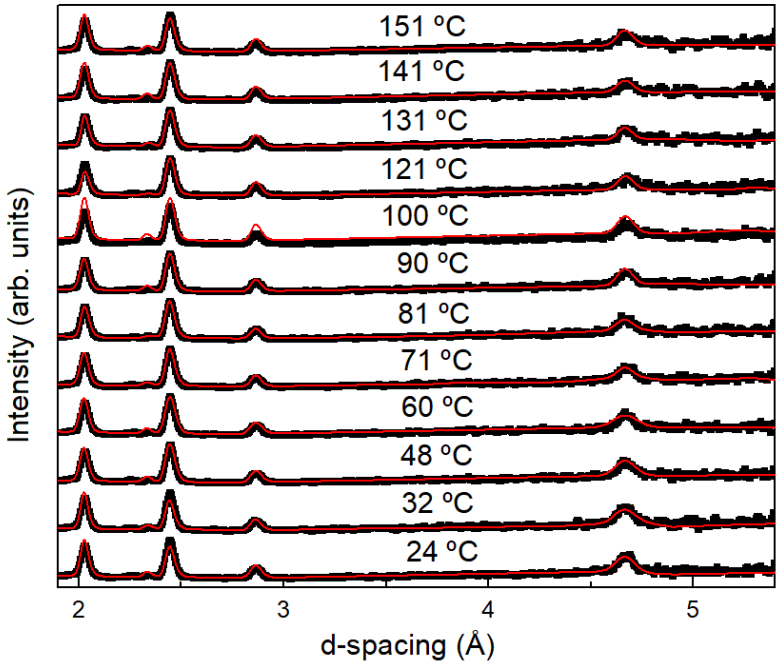


Fig. 1. Neutron diffraction patterns of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ measured at different temperatures.

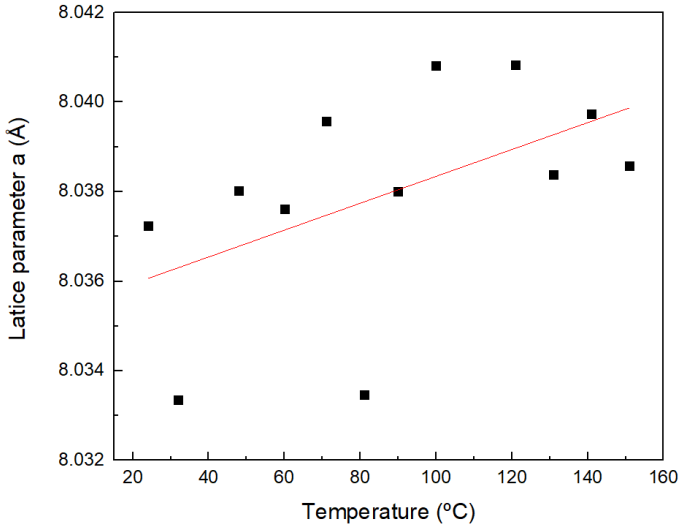
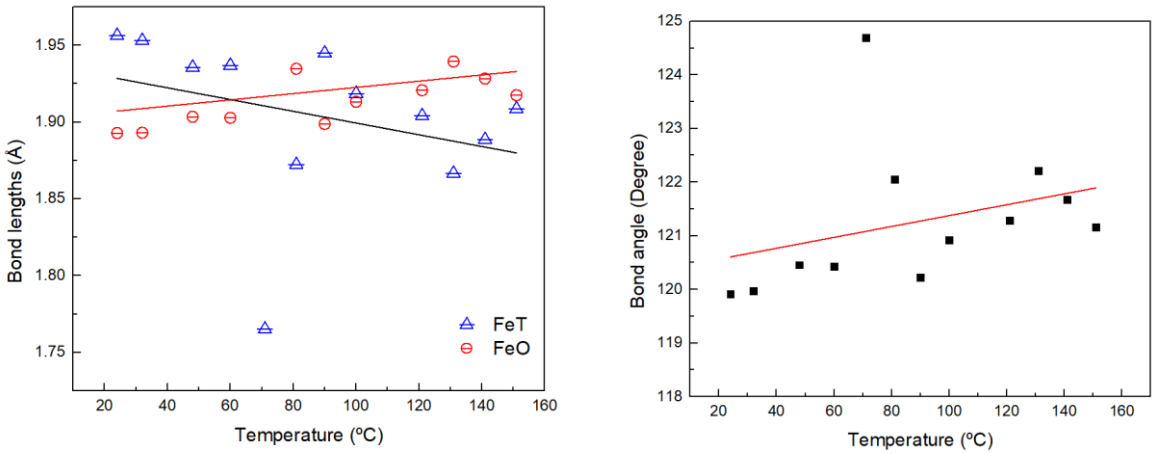


Fig 2. Temperature dependence of lattice parameter of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ spinel. The solid line is a linear fit of experimental data.

The interatomic bond lengths and angles for the tetragonal and octahedral oxygen coordination as a function of temperature are presented Fig. 3. By increasing the temperature, FeT–O bond length, which characterizes the tetrahedral oxygen coordination around A-site, decreases linearly. In contrast, the FeO–O bond length of B-site oxygen coordination increases, as shown in Fig. 3a. It is depicted in Fig. 3b that as the FeT–O–FeO bond angle increases linearly, the temperature increases.



(a) (b)

Fig 3. (a) FeT–O and FeO–O bond lengths of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ spinel and (b) FeT–O–FeO bond angle as a function of temperature. The solid lines represent linear fit of experimental data.

The temperature dependencies of the ordered Fe magnetic moments in both crystallographic sites (tetrahedral and octahedral) are shown in Fig. 4. In Fig. 5 we can observe the difference between magnetic moments at room temperature (24 ºC) and the highest temperature (151 ºC). Therefore, it is evident that with an increase in temperature there is a decrease in the magnetic moment of iron ion.

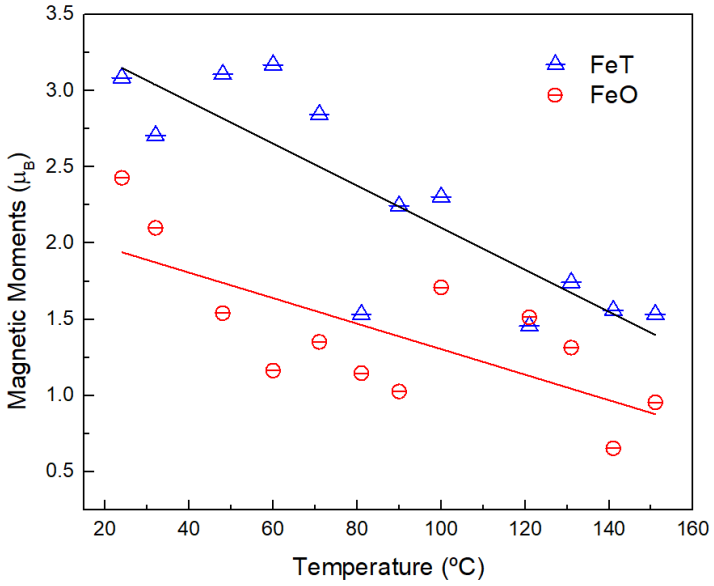


Fig 4. Temperature dependences of the magnetic moments of iron ions FeT and FeO located in tetrahedral A sites and octahedral B sites, respectively. The solid lines are linear fit of experimental data.

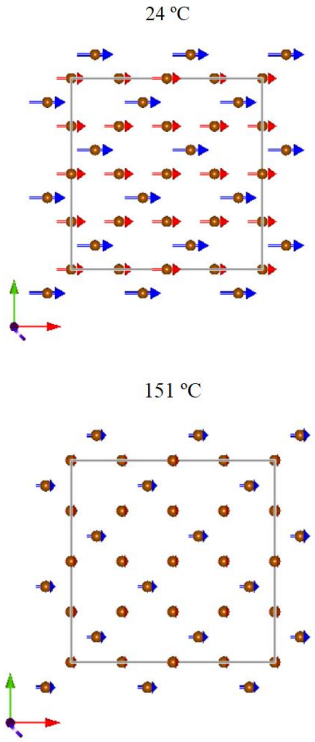


Fig 5. Representation of magnetic moment in the limits of the temperature range.

2. Pressure dependence measurements

The neutron powder diffraction patterns of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ collected at selected pressures up to 4.7 GPa and room temperature, experimental points and calculated profiles by the Rietveld method are shown in Fig. 6. The obtained pressure dependences of lattice parameters of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ are shown in Fig. 7. This parameter (and unit-cell volume) decrees with increase of pressure. No signs for pressure driven structural phase transition over the whole studied pressure range were found.

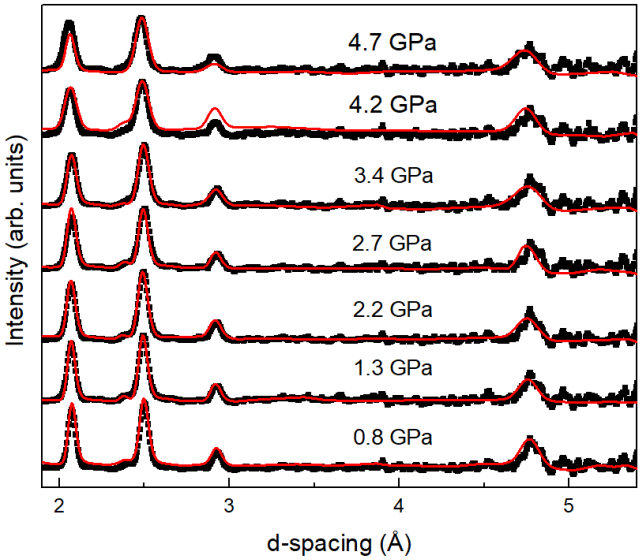


Fig 6. Neutron diffraction patterns of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ measured at different pressures.

The volume compressibility data, as illustrated in Fig. 8, was fitted by the third-order Birch–Murnaghan equation of state which is observed in Eq. (1).

$$P = \frac{3}{2} B_0 \cdot \left[\left(\frac{V}{V_0}\right)^{-\frac{7}{3}} - \left(\frac{V}{V_0}\right)^{-\frac{5}{3}} \right] \cdot \left[1 + \frac{3}{4}(B_1 - 4) \cdot \left(\left(\frac{V}{V_0}\right)^{-\frac{2}{3}} - 1 \right)\right] \quad (1)$$

V_0 is the unit cell volume at zero pressure, obtained through the intercept of the fitted graphical representation of the unit cell versus the pressure, i.e. V vs P. B_0 and B_1 are the bulk moduli such that $B_0 = -V(\frac{dP}{dV})_T$ and its pressure derivative is $B_1 = (\frac{dB_0}{dP})_T$. The fit is achieved by B_0 = 236.9 GPa and B_1 = 4.

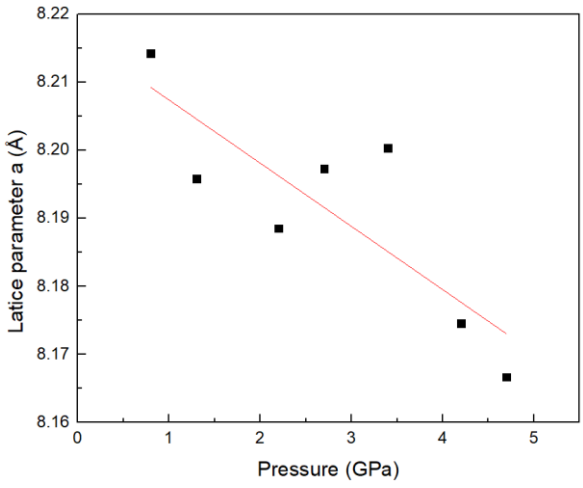


Fig 7. The pressure dependence of the cubic lattice parameter fitted by linear functions. The solid line is linear fit of experimental data.

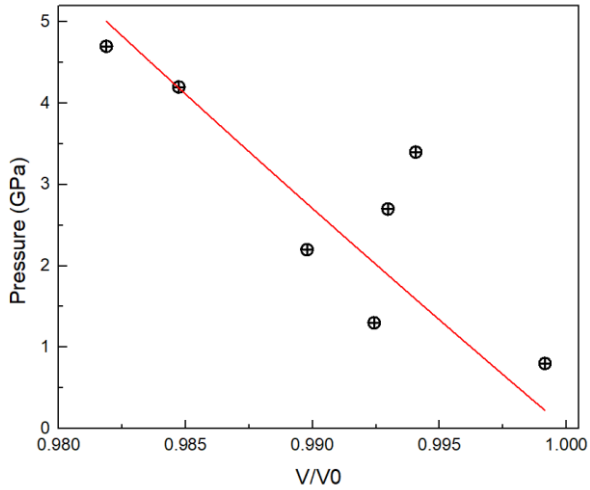
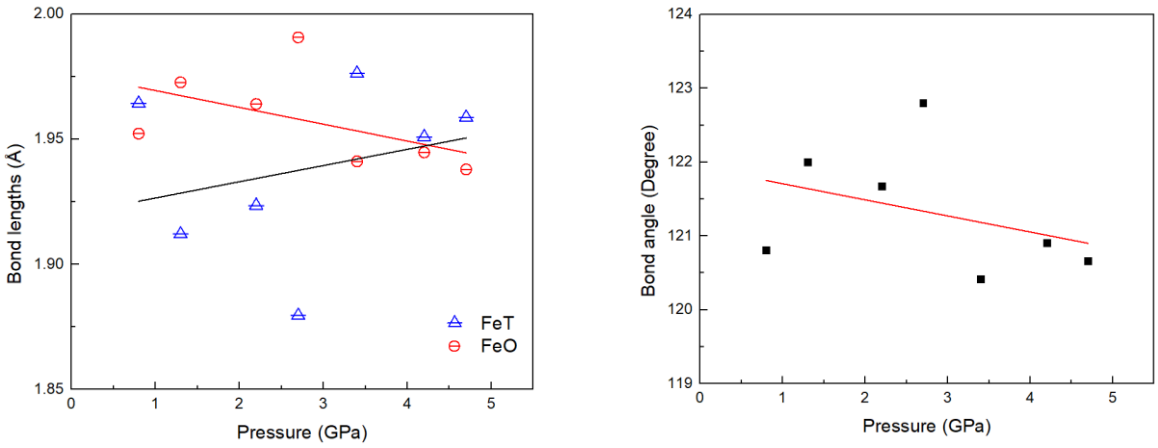


Fig 8. The volume compressibility data fitted by the third-order Birch–Murnaghan equation of state.

Under compression, the bond lengths FeT–O increase and FeO-O decrease linearly ilustrated in Fig. 9a. The FeA–O–FeB bond angle linearly decreases as pressure increases as shown in Fig. 7b.



(a) (b)

Fig 9. (a) FeT–O and FeO–O bond lengths of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ spinel as a function of temperature. (b) FeT–O–FeO bond angle as a function of temperature. The solid lines are linear fit of experimental data.

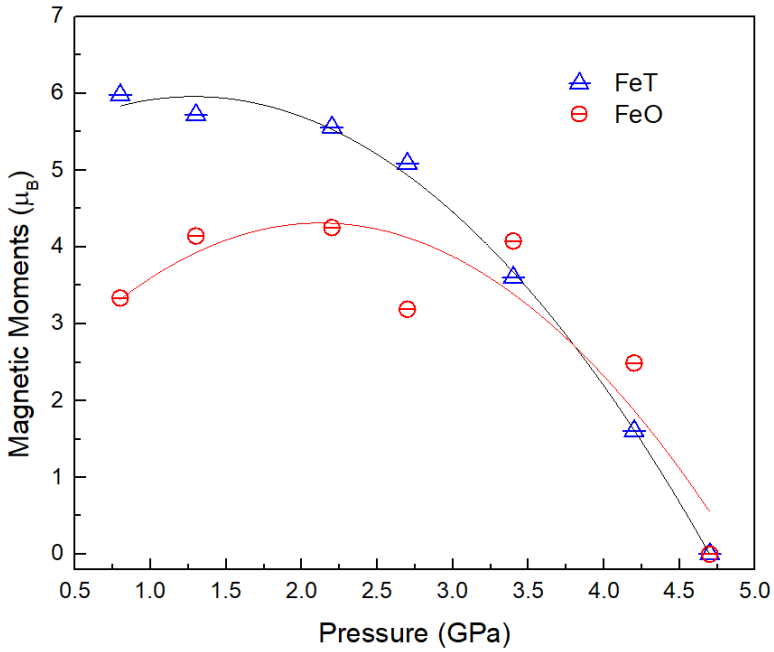


Fig 10. Pressure dependences of the FeT and FeO magnetic moments. The experimental data for FeT and FeO was fitted by polynomial.

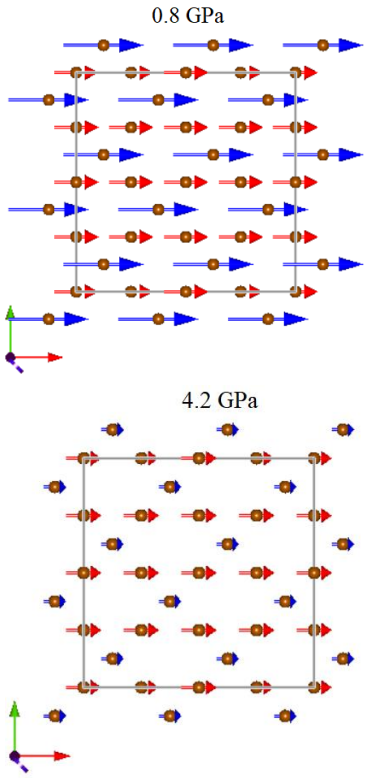


Fig 11. Representation of magnetic moment in pressure 0.8 GPa and 4.2 GPa.

As illustrated in Fig. 10 by increasing the pressure, the intensity of the magnetic peaks gradually decreases. Furthermore, it is also observed in the representation of the magnetic moments in Fig. 11. The experimental data for FeT and FeO in Fig. 10, were fitted by polynomial:

$$M(p) = A_0 + A_1 p + A_2 p^2 \quad (2)$$

In Eq. (2), FeT was obtained by $A_0 = 5.1 \pm 0.3\ \mu_B$, $A_1 = 1.3 \pm 0.2\ \mu_B/GPa$, $A_2 = -0.51 \pm 0.04\ \mu_B/GPa^2$ and for FeO we obtained $A_0 = 1.8 \pm 1.2\ \mu_B$, $A_1 = 2.4 \pm 1.0\ \mu_B/GPa$, $A_2 = -0.6 \pm 0.2\ \mu_B/GPa^2$.
After P = 4.2 GPa, the magnetic contribution to the diffraction peaks fully disappears. This fact indicates that increasing the applied pressure reduces the transition temperature T_C below the room temperature.
According to previous works [7, 9, 10], the decrease of the FeT-O-FeO bond angle will cause the weakening of the FeT-O-FeO superexchange interactions by increasing the applied pressure. At a certain pressure, the FeT-O-FeO superexchange interaction may become comparable with those of the FeT-O-FeT and FeO-O-FeO interactions. Interestingly, this should enhance the magnetic frustration in the studied compound, which accordingly will decrease sharply the magnetic ordering temperature [7, 11].

Conclusion

This work reflects the procedure to refinement neutron diffraction pattern, getting some abilities and skills in the FullProf and Diamond software. Another important aspect of this report is the type of information and results that can be obtained and the analysis that can be done from neutron diffraction pattern. Crystal and magnetic structure of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ at different pressures and temperatures were studied. The behaviour of lattice parameter, unit cell volume, interatomic distances and angles and magnetic moment with temperature and pressure were observed. By increasing the temperature and pressure, a gradual suppression of the magnetic moments of iron ions in both A and B crystallographic sites was observed. This effect corresponds to a magnetic phase transition from the ferrimagnetic state to paramagnetic.

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