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Neutron diffraction study of the pressure and temperature dependence of the crystal and magnetic structures of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ polycrystalline ferrite

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ABSTRACT

The structural and magnetic properties of doped ferrite $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ have been studied by means of the neutron diffraction method at high pressures up to 4.7 GPa and in temperature range 300–425 K. By increasing the temperature and the 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 one. The lattice parameters, interatomic bond lengths and angles, magnetic moments of iron ions as functions of temperature and pressure were obtained. Upon compression, the magnetic ordering temperature of studied ferrite decreases with a large pressure coefficient $dT_c/dP = -19(1)$ K × GPa^{-1}.

1. Introduction

The spinel-type ferrites have distinguished structural and magnetic properties [1,2]. In particular, canted antiferromagnetic, ferrimagnetic, spin glass and semi-spin glass states can be realized in these compounds [2]. 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, magneto-electronics, etc. [3]. Accordingly, a special attention is attracted to understand the structural and magnetic properties of ferrite compounds [4–6] and to develop a novel synthesis technologies to obtain definite structural and magnetic properties [2,7].

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]. In the normal ferrites with the general chemical formula AFe_2O_4, the divalent A^{2+} cations occupy only tetrahedral site A, while the Fe^{3+} cations occupy octahedral B sites only [7]. It should be noted, the $ZnFe_2O_4$ is a normal spinel ferrite at room temperature [1,7], but copper ferrite $CuFe_2O_4$ has a tetragonal structure at room temperature due to a cooperative Jahn-Teller distortion driven by Cu^{2+} cations inverse distribution into the octahedral B-site [7]. A modern scientific route is advanced synthesis of complex ferrites with controllable redistribution of iron ions between A and B sites leading to variation of the balance between complex magnetic interactions inside the magnetic structure of ferrites [8]. It is well known that the magnetic interaction J_{AB} between the magnetic moments of iron in tetrahedral A and octahedral B sublattice are stronger than those between the moments of the ions in either tetrahedral sublattice J_{AA} or octahedral sublattice J_{BB} [9]. All those magnetic interactions are antiferromagnetic, however, $|J_{AB}| \gg |J_{BB}| > |J_{AA}|$ provokes ferrimagnetism in Zn-Cu spinel ferrites compounds, leaving the A–A and B–B couplings inherently frustrated [9]. A substitution by diamagnetic ions suppresses the magnetic coupling J_{AB} and changes drastically the balance between competing interactions J_{AA} and J_{BB} [8,9], giving prerequisites to form a Yafet-Kittel triangular magnetic structure [1]. In additional, the magnetic properties of spinel ferrites can be affected by the cation–cation interactions between transition metal ions at B-sites [10]. In Zn-Cu ferrites the conduction mechanism is controlled by cation–cation [Cu–Cu] and cation–anion–cation [Fe^{3+}–O^{2-}–Fe^{3+}] electrical interactions [2]. For low Zn concentration ($x < 0.3$), the Cu–Cu

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interaction is the predominant, leading to a p-type semiconductor behavior [2,10]. As the Zn content increases the number of Fe^{3+}–O^{2-}–Fe^{3+} interactions also increase, but the [Cu–Cu] interactions consequently weaken [2], leading to a n-type semiconductor conductivity. The number of Fe^{3+}–O^{2-}–Fe^{3+} linkages in ferrite structure defines primarily the magnetic ordering temperature T_C of ferrite compound [2]. Recently, it was found, that the introduction of non-magnetic Ga^{3+} ions into the octahedral B-site decreases the number of Fe^{3+}–O^{2-}–Fe^{3+} linkages and leads to a T_C drop [10].

The observed complex interconnection between electronic and magnetic properties in the Zn-Cu-Ga ferrites makes this family of ferrites an interesting candidate for exploring the origin and the mechanism of the interplay between structural, electronic and magnetic degrees of freedom in doped spinel ferrites. Structurally, the interatomic distances and angles can control the strength of the magnetic interactions in spinel-type ferrites [11,12]. However, most of the previous studies of Zn-Cu-Ga spinel ferrites were focused on the investigation of macroscopic physical properties [6]. Further insight into the relationship between the structural properties and magnetic order in spinel ferrite can be given by studying the effect of the variation of the structural parameters on the magnetic ordering. Such change in the structural parameters can be obtained by applying a gradual increasing pressure to the ferrite unit cell. In the present work, $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ compound was chosen as a model object for a neutron diffraction study of the interplay between the crystal and magnetic structures across the paramagnetic-ferrimagnetic phase transition. The neutron diffraction measurements were performed at high pressures up to 4.7 GPa and in temperature range 300–425 K.

2. Experimental techniques

A powder sample of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ ferrite was synthesized through solid-state reactions using Fe_2O_3, ZnO, CuO and Ga_2O_3 (with purity ≥ 99.99%) as starting materials [13]. The mixture of the oxide powders was annealed at 1100 °C 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 °C for 8 h [13,14].

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 [15]. Several tiny ruby chips were placed at different points on the sample surface and the pressure was determined by a standard ruby fluorescence technique [16]. Diffraction patterns were collected at scattering angle $2\theta = 90°$ 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 425 K by means of special heater. The temperature was measured by the K-type thermocouple. The Neutron powder diffraction data were analyzed by the Rietveld method using the FULLPROF software [17].

3. Results and discussion

3.1. Temperature dependence measurements

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. At room temperature conditions this compound has the spinel-type crystal structure of $Fd\bar{3}m$ symmetry, in which the Fe atoms distribute between tetragonally coordinated A-sites and octahedrally coordinated B-sites [18].The obtained crystal structure parameters of this compound

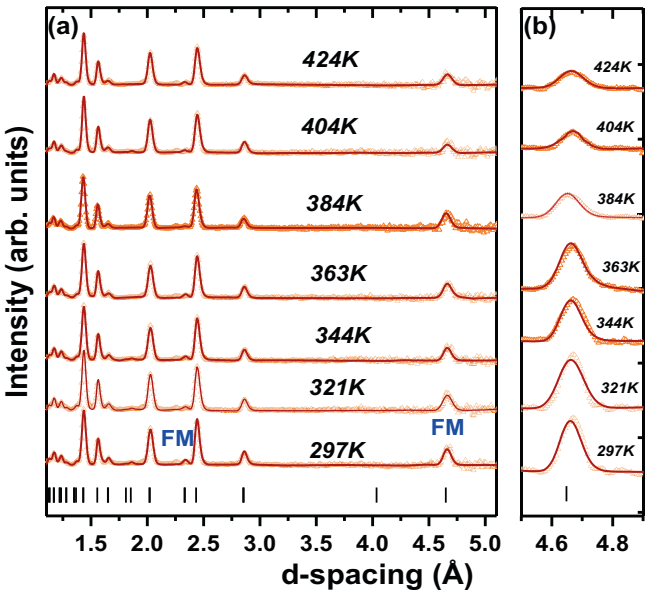

Fig. 1. (a) Neutron diffraction patterns of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ compound measured at selected temperatures up to 424 K and processed by the Rietveld method. Experimental points, calculated profiles by the Rietveld method and positions of Bragg peaks are shown. The "FM" signs the diffraction peaks with magnetic contribution. (b) Enlarged spectra region corresponded to diffraction peak with ferrimagnetic contribution.

Table 1
The crystal structural parameters of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ ferrite obtained at ambient pressures and at room temperature. In spinel-type cubic structure with $Fd\bar{3}m$ space group the Zn atoms occupy tetrahedral-coordinated A-site (*1/8; 1/8; 1/8*), Cu and Ga atoms sits in octahedral-coordinated B site (*1/2; 1/2; 1/2*). The iron ions distributed between A and B sites. The oxygen atoms O are in a position (*x; x; x*).

	Lattice parameters	
	a, Å	8.331(3)
	Atomic occupations	
A site:	*Zn*	0.30(1)
	Fe	0.68(3)
B site:	*Cu*	0.70(1)
	Fe	0.82(2)
	Ga	0.50(1)
	Calculated atomic coordinates	
	O: *x*	0.260(1)

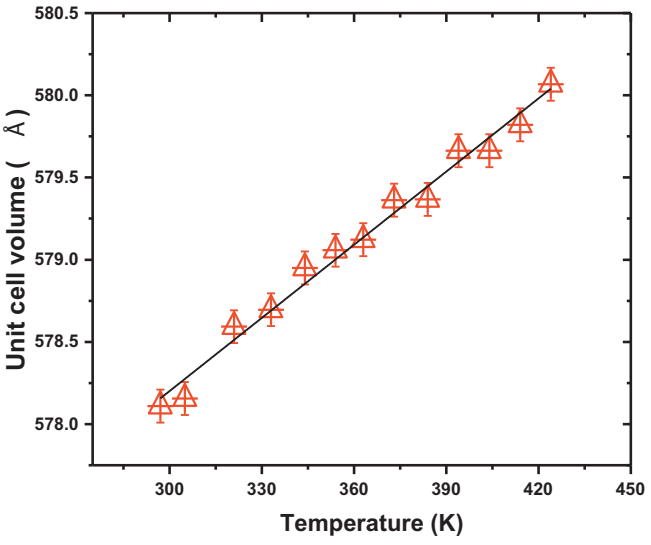

Fig. 2. Temperature dependence of the unit cell volume of $Zn_{0.3}Cu_{0.7}Fe_{1.5}Ga_{0.5}O_4$ spinel. The solid line is linear fit of experimental data.