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CRYSTAL STRUCTURE OF $Mg_3Fe_4V_6O_{24}$ STUDIED BY NEUTRON DIFFRACTION

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Abstract. A new multicomponent vanadate $Mg_3Fe_4V_6O_{24}$ containing non-magnetic magnesium(II) ions has been synthesized by the solid state reaction method using stoichiometric mixture of $FeVO_4$ and $Mg_3(VO_4)_2$ oxides. The neutron diffraction measurements have been done at 10K and 290K and the crystal structure has been analyzed to study a possible cation disorder as well as expected magnetic ordering phenomena. The distance between two neighbouring Fe(1) ions in $Mg_3Fe_4V_6O_{24}$ is significantly smaller in comparison to isostructural $Zn_3Fe_4V_6O_{24}$, whereas the distance between neighbouring Fe(2) ions is similar to what has been observed in $Zn_3Fe_4V_6O_{24}$ compound. The neutron diffraction study of the $Mg_3Fe_4V_6O_{24}$ powder has indicated that the iron(III) and magnesium(II) ions are not disordered in the investigated structure and there is no magnetic ordering down to the temperature of 10K.

1. INTRODUCTION

Multicomponent vanadates $M_2FeV_3O_{11}$ and $M_3Fe_4V_6O_{24}$ (where M – metal ion) have shown very interesting physical properties, especially connected with the cation disorder phenomena [1-7]. The XRD and neutron diffraction studies of the $M_2FeV_3O_{11}$ (M(II)=Zn, Mg) compounds have shown that the iron(III) and metal(II) ions were disordered in their corresponding subsystems, and the distribution at the octahedral and the trigonal bipyramidal sites was non-statistical [3-5]. On the other hand, the neutron diffraction study of the $Zn_3Fe_4V_6O_{24}$ compound has not shown any cation disorder [7]. Neutron diffraction method, in contrast to XRD, has revealed the existence of manganese and iron ions disorder at the M(2), M(3) and M(4) sites in the $Mn_3Fe_4V_6O_{24}$ structure [8]. Electron paramagnetic study of various $M_3Fe_4V_6O_{24}$ (M(II)=Mg, Zn, Mn, Cu, Co) compounds at room temperature has revealed large differences in the magnetic response of those samples in which two magnetic ions are present in the lattice [9].

This work presents the results of the neutron diffraction study of $Mg_3Fe_4V_6O_{24}$ obtained by the solid state reaction of $FeVO_4$ and $Mg_3(VO_4)_2$. The crystal structure of $Mg_3Fe_4V_6O_{24}$ is analyzed and compared to the isostructural $M_3Fe_4V_6O_{24}$ (M=Zn and Mn) compounds with special attention to the magnetic properties, the thermal expansion coefficients and the metal-oxygen bond angles and lengths.

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2. EXPERIMENTAL

Polycrystalline samples of $Mg_3Fe_4V_6O_{24}$ (or $Mg_3Fe_4(VO_4)_6$) were obtained from the solid-state reaction between 80 mol.% $FeVO_4$ and 20 mol.% $Mg_3(VO_4)_2$, according to the equation [10]:

$$4\,FeVO_4 + Mg_3(VO_4)_2 = Mg_3Fe_4V_6O_{24}.$$

The crystal structure of the $Mg_3Fe_4V_6O_{24}$ compound was investigated by the neutron powder diffraction method using a high luminosity DN-2 time-of-flight powder diffractometer [11] on the IBR-2 pulsed reactor at the FLNF Frank Laboratory of the Joint Institute of Nuclear Research (JINR), Dubna (Russia). The neutron diffraction patterns were measured with the resolution determined by the width of the pulse from a neutron source, $\Delta d/d$=0.01 in the range of interplanar spacings d_{hkl} from 1 to 20 Å. The diffraction patterns were collected employing approximately 10 g of the sample, enclosed in a thin wall aluminum cylindrical container of 8 mm in diameter. The counting time was 15 h for every point at a specific temperature. The diffraction patterns were obtained at two temperatures: 10K and 290K. The difference patterns do not show any magnetic contribution to the diffraction. Structure refinement was carried out using a computer program [12] based on the multi-phase Rietveld analysis method. X-ray diffraction data for β-$Cu_3Fe_4(VO_4)_6$ was used as a starting model for Rietveld refinement [1,12].

3. RESULTS AND DISCUSSION

$Mg_3Fe_4V_6O_{24}$ compound is a homeotype of β-$Cu_3Fe_4V_6O_{24}$. The crystal structure of $M_3Fe_4V_6O_{24}$ is build up from $M(1)O_6$ polyhedra, $M(2)O_5$ trigonal bipyramids, $M(3)O_6$ and $M(4)O_6$ octahedra and isolated VO_4 tetrahedra. Fe_2O_{10} octahedral dimers alternate with $M(2)O_5$ bipyramids to form edge-sharing chains (Fe(1) and Fe(2) are in position M(3) and M(4), respectively). The $M(1)O_6$ octahedra are located between the chains and share corners with both the $M(2)O_5$ and Fe_2O_{10} units.

The projection of the structure of $Mg_3Fe_4V_6O_{24}$ along [100] axis is presented in Fig. 1. As shown in this figure, M(1) atoms are placed within the [100] tunnels. The distance between M(1) ions is $d_{Mg(1)-Mg(1)}$=6.685 Å in $Mg_3Fe_4(VO_4)_6$ and for $Zn_3Fe_4(VO_4)_6$ the value of $d_{Zn(1)-Zn(1)}$=6.682 Å is similar [7]. However, the distance between Cu(1) ions ($d_{Cu(1)-Cu(1)}$=6.600 Å) in a homeotype $Cu_3Fe_4(VO_4)_6$ compound is essentially different [1]. Bipyramid $M(2)O_5$ is connected with $M(1)O_6$ polyhedron, with one Fe(1)octahedral dimer and one Fe(2) dimer

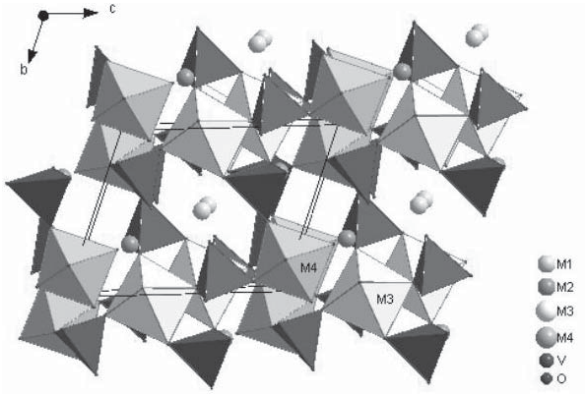


Fig. 1. $Mg_3Fe_4V_6O_{24}$ structure viewed in the [100] direction.

through the O(11) atom, O(7)-O(6) edge and O(4)-O(8) edge, respectively.

Fe(1) and Fe(2) octahedra form the edge-sharing dimeric clusters. However, their environment of vanadium VO_4 tetrahedra is different. The $Fe(2)_2O_{10}$ octahedral dimers are surrounded by ten isolated VO_4 tetrahedra, sharing each one corner with the Fe(2) dimer, and therefore they form a $Fe(2)_2O_{10}$ unit. Only eight VO_4 tetrahedra build up a $Fe(1)_2O_{10}$ unit. They are linked to the Fe(1) dimer, since two $V(2)O_4$ share two vertices, instead of one, with the dimer. The Fe(1)-Fe(1) distance $d_{Fe(1)-Fe(1)}$=3.066 Å is less than even the Fe(2)-Fe(2) distance, $d_{Fe(2)-Fe(2)}$=3.193 Å, thus the difference $\Delta d = d_{Fe(1)-Fe(1)} - d_{Fe(2)-Fe(2)}$=-0.127 Å. For the β-$Cu_3Fe_4V_6O_{24}$ and $Zn_3Fe_4V_6O_{24}$ compounds, the above distances are the following [1,7]: $d_{Fe(1)-Fe(1)}$=3.095Å and $d_{Fe(2)-Fe(2)}$=3.152 Å, respectively, with differences Δd=-0.06 Å for β-$Cu_3Fe_4V_6O_{24}$ and $d_{Fe(1)-Fe(1)}$=3.117Å and $d_{Fe(2)-Fe(2)}$=3.192 Å, respectively, with difference Δd=-0.075 Å for $Cu_3Fe_4V_6O_{24}$. The value of Δd is almost two times greater for sample with Mg(II) than for Zn(II) ions while the distance $d_{Fe(2)-Fe(2)}$ is similar for both samples. Essential differences are observed for the distances between Fe(1) ions, $d(Mg)_{Fe(1)-Fe(1)} - d(Zn)_{Fe(1)-Fe(1)}$=-0.051 Å, and the distances between Fe(2) ions $d(Mg)_{Fe(2)-Fe(2)} - d(Zn)_{Fe(2)-Fe(2)}$=-0.001 Å.

$V(1)O_4$ tetrahedra connect different Fe(1) dimers through their corners. $Fe(1)_2O_{10}$ units form chains parallel to the **a** axis. $Fe(2)_2O_{10}$ units are linked to each other through $V(2)O_4$ and $V(3)O_4$ tetrahedra. They build up layers in the (**a, b**) plane. The distance between neighboring layers of $Fe(2)_2O_{10}$ units is equal to **c**.

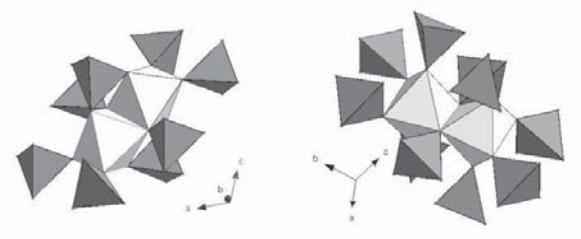


Fig. 2. Vanadium tetrahedral arrangement of the Fe1 (left) and Fe2 (right) dimers.

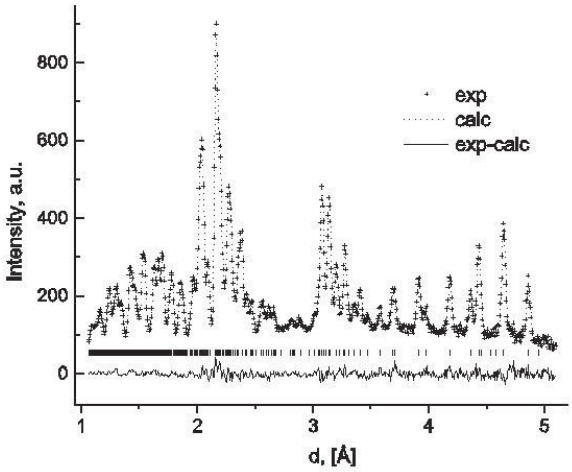


Fig. 3. Observed, calculated (χ^2=1.82) spectra and the difference pattern for $Mg_3Fe_4V_6O_{24}$.

Table 1. Structure parameters for $Mg_3Fe_4V_6O_{24}$ obtained from the neutron diffraction (at 10K and 290K) and XRD at room temperature. For comparison, similar data are given for $Zn_3Fe_4V_6O_{24}$ and β-$Cu_3Fe_4V_6O_{24}$.

Parameter	T=290K	T=10K	XRD [10]	$Zn_3Fe_4V_6O_{24}$ [10]	β-$Cu_3Fe_4V_6O_{24}$ [1]
System	triclinic	triclinic	Triclinic	triclinic	triclinic
Space group	*P*-1 (no.2)	*P*-1 (no.2)	*P*-1(no.2)	*P*-1(no.2)	*P*-1(no.2)
fw	985.94	985.94	985.94	1109.19	1103.66
a [E]	6.685(1)	6.686(1)	6.678(5)	6.681(1)	6.600(3)
b [E]	8.025(1)	8.021(1)	8.027(4)	8.021(2)	8.048(4)
c [E]	9.769(1)	9.775(1)	9.759(7)	9.778(4)	9.759(5)
α [°]	105.14(1)	105.13(1)	105.16(8)	105.25(4)	106.08(3)
β [°]	105.07(1)	105.09(1)	104.95(9)	105.00(4)	103.72(3)
γ [°]	101.72(1)	101.79(1)	101.91(9)	102.20(4)	102.28(2)
V [E^3]	467.38(9)	467.25(8)	466.3	465.8	461.8
Z	1	1	1	1	1
d_{calc} [g/cm^3]	3.50	3.50	3.51	3.95	3.97
R_p	2.81	2.32	-	-	-
R_w	2.22	1.56	-	-	-
χ^2	1.82	1.62	-	-	-

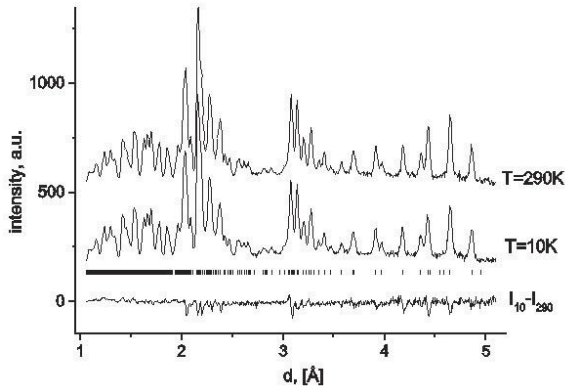
$$\chi^2 = \sum w(I_e - I_c)^2; R_w = \left[\sum w(I_e - I_c)^2 / \sum wI_e^2\right]^{-1/2}; R_p \sum \|I_e - I_c\| / \sum |I_e|.$$

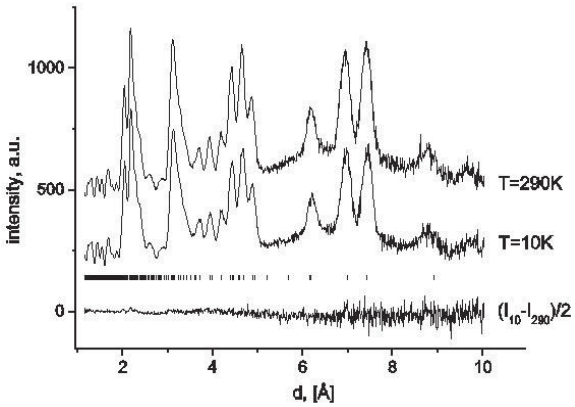
$Mg_3Fe_4V_6O_{24}$ compound crystallizes in the triclinic system. Parameters of the unit cell determined from neutron diffraction (at both temperatures: 10K and 290K) and XRD analysis are presented in Table 1. For comparison, literature data for similar $Zn_3Fe_4V_6O_{24}$ and β-$Cu_3Fe_4V_6O_{24}$ compounds are presented. The values of the unit cell parameters increase with increasing temperature and some discrepancy is observed between the neutron diffraction and XRD data (Table 1). The bulk crystal unit cells parameters have been changed by the temperature change in the following way: Δa_T=-0.001 Å,

Table 2. Atomic coordinates for $Mg_3Fe_4V_6O_{24}$ obtained from refinement of neutron diffraction data.

atom		occ.	T=290K			T=10K		
			x	y	z	X	Y	z
M(1)	1g	1.0	0	1/2	S	0	S	1/2
M(2)	2i	2.0	0.721(3)	0.718(2)	0.209(1)	0.727(3)	0.720(2)	0.206(1)
M(3)	2i	2.0	0.382(2)	0.952(2)	0.606(1)	0.382(1)	0.951(1)	0.612(1)
M(4)	2i	2.0	0.036(2)	0.206(1)	0.009(1)	0.043(1)	0.210(1)	0.014(1)
V(1)	2i	2.0	0.8917	0.8998	0.6644	0.8917	0.8998	0.6644
V(2)	2i	2.0	0.2208	0.6546	0.2699	0.2208	0.6546	0.2699
V(3)	2i	2.0	0.5903	0.2681	0.1236	0.5903	0.2681	0.1236
O(1)	2i	2.0	0.096(3)	0.057(2)	0.148(2)	0.087(2)	0.054(2)	0.148(1)
O(2)	2i	2.0	0.573(2)	0.129(2)	0.224(2)	0.567(2)	0.125(2)	0.218(1)
O(3)	2i	2.0	0.187(3)	0.431(2)	0.191(2)	0.197(2)	0.430(2)	0.189(2)
O(4)	2i	2.0	0.997(2)	0.282(2)	0.824(1)	0.988(2)	0.282(1)	0.821(1)
O(5)	2i	2.0	0.239(2)	0.794(2)	0.970(2)	0.232(2)	0.794(2)	0.976(1)
O(6)	2i	2.0	0.872(3)	0.958(2)	0.349(2)	0.871(3)	0.953(2)	0.344(2)
O(7)	2i	2.0	0.526(2)	0.230(2)	0.729(2)	0.523(2)	0.238(2)	0.731(2)
O(8)	2i	2.0	0.342(3)	0.246(2)	0.984(2)	0.346(2)	0.239(2)	0.980(2)
O(9)	2i	2.0	0.326(2)	0.035(2)	0.423(2)	0.332(2)	0.026(2)	0.427(1)
O(10)	2i	2.0	0.218(3)	0.680(2)	0.460(2)	0.221(3)	0.676(2)	0.458(1)
O(11)	2i	2.0	0.724(2)	0.501(2)	0.248(1)	0.710(2)	0.506(1)	0.251(1)
O(12)	2i	2.0	0.120(2)	0.289(1)	0.409(1)	0.119(2)	0.297(1)	0.407(1)

M(1)=Mg; M(2)=Mg; M(3)=Fe; M(4)=Fe.





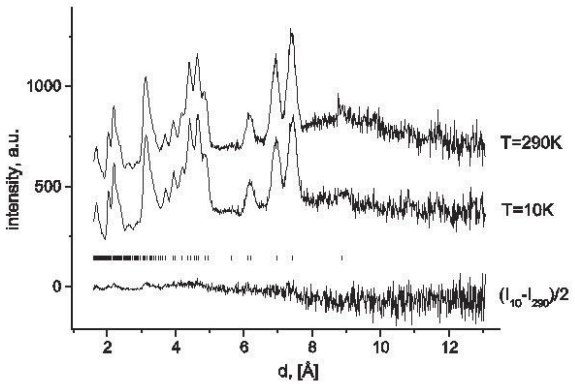


Fig. 4. Neutron diffraction spectra of $Mg_3Fe_4V_6O_{24}$ obtained at temperatures 10K and 290K and the difference of both spectra.

Δb_T=0.004 Å, Δc_T=-0.006 Å, and the volume change ΔV_T =0.13 Å^3. As could be seen from these values, the thermal expansion processes is anisotropic, being the largest in the **c** direction. The three discussed compounds show similar value of the crystal structure parameters. The final refined atomic coordinates at both temperatures are shown in Table

Table 3. Selected bond distances and angles for $Mg_3Fe_4V_6O_{24}$.

Bond (E)			
M(1) - O(12)	2.11(1) ґ 2	M(4) - O(8)	2.09(2)
M(1) - O(10)	2.02(2) ґ 2	M(4) - O(3)	2.02(3)
M(1) - O(11)	2.67(1) ґ 2	M(4) - O(1)	2.05(2)
M(2) - O(11)	1.88(2)	V(1) - O(12)	1.48(1)
M(2) - O(7)	1.98(2)	V(1) - O(6)	1.81(2)
M(2) - O(4)	2.00(2)	V(1) - O(1)	1.75(2)
M(2) - O(8)	1.93(2)	V(1) - O(9)	1.74(2)
M(2) - O(6)	1.92(3)	V(2) - O(3)	1.70(2)
M(3) - O(2)	1.92(2)	V(2) - O(7)	1.75(2)
M(3) - O(6)	2.08(2)	V(2) - O(10)	1.82(2)
M(3) - O(9)	2.04(2)	V(2) - O(4)	1.75(2)
M(3) - O(9)	2.14(2)	V(3) - O(5)	1.71(1)
M(3) - O(10)	2.14(3)	V(3) - O(2)	1.67(2)
M(3) - O(7)	2.11(2)	V(3) - O(11)	1.82(2)
M(4) - O(5)	1.90(2)	V(3) - O(8)	1.80(2)
M(4) - O(4)	2.02(2)	M(3) - M(3)	3.07(2)
M(4) - O(1)	2.01(2)	M(4) - M(4)	3.19(2)
angle (°)			
O(12) - M(1) - O(12)	180.0	O(11) - M(2) - O(4)	86.2(9)
O(12) - M(1) - O(10)	91.1(7) × 2	O(11) - M(2) - O(8)	127.3(9)
O(12) - M(1) - O(10)	88.9(7) × 2	O(11) - M(2) - O(6)	126.3(9)
O(12) - M(1) - O(11)	99.5(5) × 2	O(7) - M(2) - O(4)	168(2)
O(12) - M(1) - O(11)	80.5(5) × 2	O(7) - M(2) - O(8)	101.7(9)
O(10) - M(1) - O(10)	180.0	O(7) - M(2) - O(6)	82.6(9)
O(10) - M(1) - O(11)	84.8(6) × 2	O(4) - M(2) - O(8)	80.6(9)
O(10) - M(1) - O(11)	95.2(6) × 2	O(4) - M(2) - O(6)	85.5(9)
O(11) - M(1) - O(11)	180.0	O(8) - M(2) - O(6)	103.3(9)
O(11) - M(2) - O(7)	101.1(9)		

2. The coordinates of vanadium given in the Table 2 are taken from X-ray data for β-$Cu_3Fe_4V_6O_{24}$ since the vanadium position data are determined with a large uncertainty by the neutron diffraction method because of small vanadium scattering amplitude.

The bond lengths and angles for the $Mg_3Fe_4V_6O_{24}$ compound at both investigated temperatures as well as the average values for the system β-$Cu_3Fe_4V_6O_{24}$ could be calculated and compared [1]. The temperature dependence of the metal-oxygen lengths for $Mg_3Fe_4V_6O_{24}$ could be calculated from the 290K (see Table 3) and 10K measurements and the following values are obtained:

$$\Delta d_{1T} = \langle M(1)-O\rangle_{[4+2]}(290) - \langle M(1)-O\rangle_{[4+2]}(10) = 0.004\text{Å};$$

$$\Delta d_{2T} = \langle M(1)-O\rangle_{[4]}(290) - \langle M(1)-O\rangle(10) = 0.024\text{Å};$$

$$\Delta d_{3T} = \langle M(2)-O\rangle(290) - \langle M(2)-O\rangle(10) = 0.023\text{Å};$$

$$\Delta d_{4T} = \langle M(3)-O\rangle(290) - \langle M(3)-O\rangle(10) = -0.010\text{Å};$$

$$\Delta d_{5T} = \langle M(4)-O\rangle(290) - \langle M(4)-O\rangle(10) = 0.001\text{Å}.$$

The thermal expansion process changes mostly the distances involving the M(1) and M(2) positions.

The neutron diffraction study of powder of $Mg_3Fe_4V_6O_{24}$ has indicated that the iron(III) and magnesium(II) ions are not disordered in the structure, in contrast to other compounds in the

$M_2FeV_3O_{11}$ system where essential cation disorder phenomena have been observed [3,4,5].

4. CONCLUSIONS

The sample $Mg_3Fe_4V_6O_{24}$ with non-magnetic magnesium(II) ions has been prepared for study of the magnetic and crystal structure and to compare them with other isostructural system containing non-magnetic Zn(II) ions. In both cases of the compounds with non-magnetic metal(II) ions no magnetic ordering has been observed down to 10K, but the distance between Fe(1) ions is essentially different while the distance between Fe(2) ions has the same value in both structures. The iron(III) and magnesium(II) ions are not disordered in their structure and one can speculate that oxygen deficiency and oxygen disordering might be responsible.

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