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# Neutron diffraction study of $Mn_3Fe_4V_6O_{24}$

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$Mn_3Fe_4V_6O_{24}$ compound was prepared using the solid-state reaction method. The magnetic and crystal structural studies were carried out by using neutron diffraction methods at the temperatures of 10 and 290 K. Down to 10 K no long-range magnetic order was observed. Essential differences in the positions of metal ions were observed as compared to similar systems ($\beta$-$Cu_3Fe_4V_6O_{24}$ and $Zn_3Fe_4V_6O_{24}$) investigated by X-ray and neutron diffraction methods. In this system, a disordering process involving iron and manganese atoms in M(2), M(3), M(4) cation sites was found, which could be responsible for the significant differences in the physical properties observed for this type of compound.

*Key words: neutron diffraction; crystal structure*

## 1. Introduction

The knowledge of the crystallographic and magnetic structures of multi -component vanadate oxide compounds is very important for better understanding their interesting physical properties [1–6]. Neutron diffraction studies of $Zn_2FeV_3O_{11}$ and $Mg_2FeV_3O_{11}$ compounds have shown that iron(III) and zinc/magnesium ions are disordered in their corresponding sublattices, and that the distributions on octahedral and trigonal bipyramidal sites are non-statistical [3, 5]. The $M_2FeV_3O_{11}$ (M = Zn and Mg) compounds synthesized in the reaction of $FeVO_4$ with pyrovanadates $M_2V_2O_7$ exhibited disorder in cation sites [2, 3, 5]. Recently, $M_3Fe_4V_6O_{24}$ (M = Zn, Co(II),

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Mg, Mn) compounds have been obtained as the products of reactions between $FeVO_4$ and $M_2V_2O_8$. These compounds crystallize in the triclinic space group $P\overline{1}$ [1, 7–9]. X-ray analysis has not revealed any disorder among iron(III) and divalent (Zn, Co, Mg) ions in the compounds.

The aim of this paper is to report a study of the crystal and magnetic structures of $Mn_3Fe_4V_6O_{24}$ compound, which was prepared in reaction between the MnO, $Fe_2O_3$, and $V_2O_5$. Neutron diffraction was used, and special care was taken to search for possible disorder in the cation sites.

## 2. Experimental

A powder sample of $Mn_3Fe_4V_6O_{24}$ was synthesized by the solid-state reaction method from appropriate metal oxides. MnO, $V_2O_5$, and $Fe_2O_3$ powders where mixed in a 3:3:2 molar ratio, according to the following reaction:

$$3MnO + 3V_2O_5 + 2Fe_2O_3 \rightarrow Mn_3Fe_4V_6O_{24}$$

The powders were mixed, pressed into pellets, and calcinated in air at 600 °C for 24 h, at 700 °C for 24 h, and at 750 °C for 24 h (twice). After each heating stage, the sample was slowly cooled down to room temperature, ground, and analysed by the differential thermal analysis (DTA) and X-ray diffraction (XRD), until the formation of a single phase sample could be verified. The obtained compound crystallized in the triclinic space group $P\overline{1}$, forming a dark brown-coloured powder, with its melting point at 1163 K, as determined by DTA.

The crystal structure of the $Mn_3Fe_4V_6O_{24}$ was investigated by the neutron powder diffraction method using a high luminosity DN-2 time-of-flight powder diffractometer on a IBR-2 pulsed reactor at the FLNF Frank Laboratory of the Joint Institute of Nuclear Research (JINR) in Dubna, Russia. The neutron diffraction patterns were measured with a resolution determined by the width of the pulse from a neutron source, $\Delta d/d = 0.01$, with interplanar spacing $d_{hkl}$ ranging from 1 to 20 Å. The diffraction patterns were collected by using approximately 10 g of the investigated sample, enclosed in a thin-walled aluminium cylindrical container 8 mm in diameter. The counting time was 15 h for each temperature. Diffraction patterns were obtained at 10 K and 290 K, and analysed by the program MRIA (Multi-Phase Rietveld Analysis) [10] using X-ray diffraction data for $\beta$-$Cu_3Fe_4(VO_4)_6$ as a starting model for Rietveld refinement [1, 11].

## 3. Results and discussion

Figure 1 shows the neutron diffraction spectra of different profiles obtained at 10 and 290 K for the $Mn_3Fe_4V_6O_{24}$ compound. The diffraction patterns did not show any long-range magnetic ordered state at the investigated temperatures. Figure 2 presents a neutron diffraction spectrum of $Mn_3Fe_4V_6O_{24}$ and a simulated spectrum calculated by the program MRIA ($\chi^2 = 1.75$). A very good agreement was obtained between the experimental and calculated spectra.

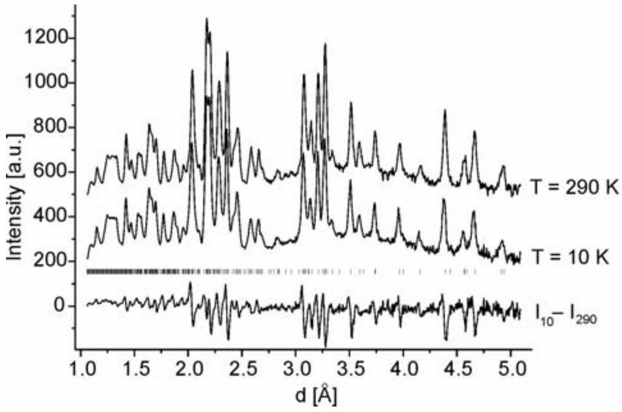

Fig. 1. Experimental neutron diffraction spectra of $Mn_3Fe_4V_6O_{24}$ obtained in the range of $d_{hkl}$ up to 11 Å at 290 K, 10 K and the difference of their intensities

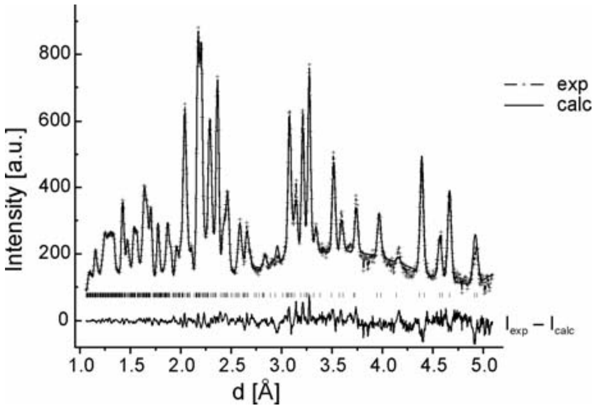

Fig. 2. Neutron diffraction spectrum of $Mn_3Fe_4V_6O_{24}$ and a simulated spectrum obtained by the MRIA program ($\chi^2 = 1.75$) at 290 K

$Mn_3Fe_4V_6O_{24}$ is a homeotype of $\beta$-$Cu_3Fe_4V_6O_{24}$ [11], since the structure is built 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) at the M(3) and M(4) positions, respectively). The $M(1)O_6$ octahedra are located between chains and share corners with both $M(2)O_5$ and $Fe_2O_{10}$ units.

Figure 3 presents a projection of the structure along the [100] axis. M(1) ions are located within the [100] tunnels. The distance between M(1) ions is $d_{M(1)–M(1)} = 6.703$ Å in the $Mn_3Fe_4(VO_4)_6$ compound. The $M(2)O_5$ bipyramid is connected with the $M(1)O_6$ polyhedron, with one Fe(1) octahedral dimer and one Fe(2) dimer through the O(11) atom, O(7)–O(6) edge, and O(4)–O(8) edge, respectively (Fig. 4).

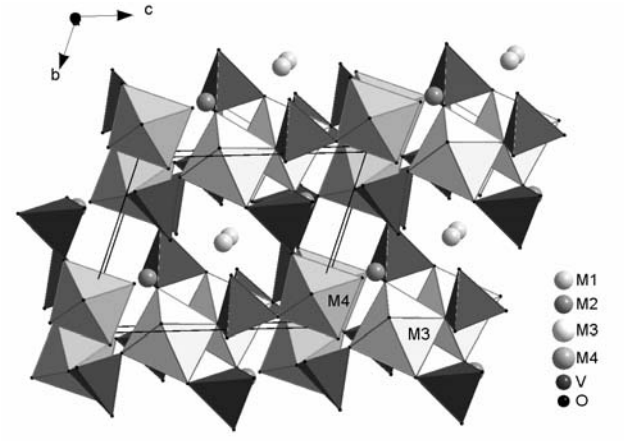

Fig. 3. Crystal structure of $Mn_3Fe_4V_6O_{24}$ viewed along the *a* axis.
See bottom of Table 2 for explanation of the symbols

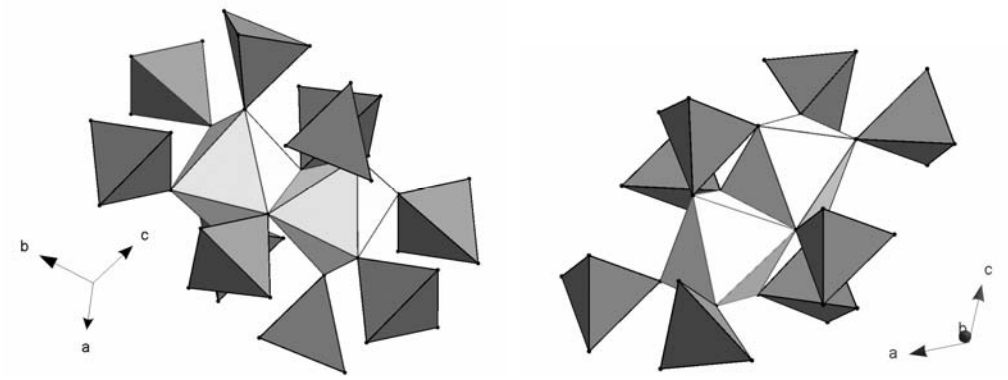

Fig. 4. Vanadium tetrahedral arrangement of the Fe1 (left) and Fe2 (right) dimers

Fe(1) and Fe(2) octahedra form edge-sharing dimeric clusters. Their environment of vanadium tetrahedra,$VO_4$, however, is different. $Fe(2)_2O_{10}$ octahedral dimers are surrounded by ten isolated $VO_4$ tetrahedra, each sharing 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 with the dimmer instead of one. The Fe(1)–Fe(1) distance $d_{Fe(1)–Fe(1)}$ = 3.330 Å is even longer than the Fe(2)–Fe(2) distance, $d_{Fe(2)–Fe(2)}$ = 3.148 Å, thus the difference $\Delta d = d_{Fe(1)–Fe(1)} - d_{Fe(2)–Fe(2)}$ = 0.182 Å. For the $\beta$-$Cu_3Fe_4V_6O_{24}$ compound, the above distances are [10]: $d_{Fe(1)–Fe(1)}$ = 3.095Å and $d_{Fe(2)–Fe(2)}$ = 3.152 Å, respectively, with a differences of *d* equal to –0.06 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 (Fig. 5). $Fe(2)_2O_{10}$ units are linked to each other through $V(2)O_4$ and $V(3)O_4$ tetrahedra. They build up layers in the *ab* plane. The distance between neighbouring layers of $Fe(2)_2O_{10}$ units is equal to *c*.

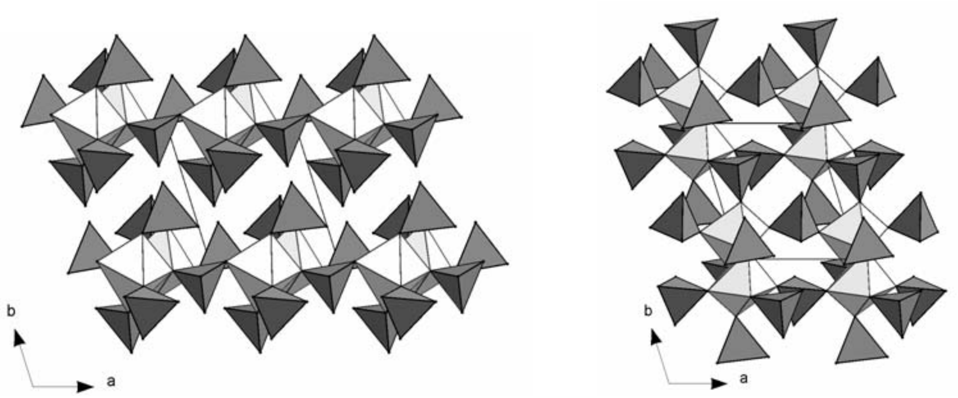

Fig. 5. Chains of $Fe(1)_2O_{10}$ units (left) and linked $Fe(2)_2O_{10}$ units in the *ab* plane (right)

Table 1. Crystallographic data for $Mn_3Fe_4V_6O_{24}$ obtained from neutron diffraction (at 10 K and 290 K) and XRD at room temperature.
For comparison, similar data for $Zn_3Fe_4V_6O_{24}$ and $\beta$-$Cu_3Fe_4V_6O_{24}$ are given

| Parameter | $T$ = 290 K | T = 10 K | XRD [1] | $Zn_3Fe_4V_6O_{24}$ [7] | $\beta$-$Cu_3Fe_4V_6O_{24}$ [11] |
|---|---|---|---|---|---|
| System | triclinic | | | | |
| Space group | *P*–1 (No. 2) | | | | |
| fw | 1077.84 | 1077.84 | 1077.84 | 1109.19 | 1103.66 |
| $a$ [Å] | 6.7041(5) | 6.7014(5) | 6.703(2) | 6.681(1) | 6.600(3) |
| $b$ [Å] | 8.1487(7) | 8.1410(7) | 8.137(1) | 8.021(2) | 8.048(4) |
| $c$ [Å] | 9.8121(7) | 9.8006(7) | 9.801(2) | 9.778(4) | 9.759(5) |
| $\alpha$ [°] | 105.51(1) | 105.47(1) | 105.56(1) | 105.25(4) | 106.08(3) |
| $\beta$ [°] | 105.54(1) | 105.66(1) | 105.58(2) | 105.00(4) | 103.72(3) |
| $\gamma$ [°] | 102.37(1) | 102.41(1) | 102.35(1) | 102.20(4) | 102.28(2) |
| $V$ [Å$^3$] | 473.4(1) | 471.9(1) | 471.9(2) | 465.8 | 461.8 |
| Z | 1 | 1 | 1 | 1 | 1 |
| $d_{calc}$ [g/cm$^3$] | 3.78 | 3.78 | 3.79 | 3.95 | 3.97 |
| $R_p$ | 2.96 | 2.78 | – | – | – |
| $R_w$ | 1.94 | 1.60 | – | – | – |
| $\chi^2$ | 1.70 | 1.60 | – | – | – |

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

$Mn_3Fe_4V_6O_{24}$ crystallizes in a triclinic system. The parameters of the unit cell determined from neutron diffraction (at both investigated temperatures, 10 K and 290 K) and XRD analysis are presented in Table 1, together with literature data for the $Zn_3Fe_4V_6O_{24}$ and $\beta$-$Cu_3Fe_4V_6O_{24}$ compounds. The final refined atomic coordinates and the occupancy factors are shown in Table 2. 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). It is suggested that the analysis of the neutron diffraction data is more accurate. The three discussed compounds exhibit similar values of the crystal structure parameters.

Table 2. Atomic coordinates of $Mn_3Fe_4V_6O_{24}$ obtained from refined neutron diffraction data

| Atom | Site occupancy | | *T* = 290 K | | | *T* = 10 K | | |
|---|---|---|---|---|---|---|---|---|
| | | | *x* | *y* | *z* | *x* | *y* | *z* |
| M(1) | 1g | 1.0 | 0 | 1/2 | 1/2 | 0 | 1/2 | 1/2 |
| M(2) | 2i | 2.0 | 0.791(8) | 0.725(8) | 0.232(5) | 0.741(8) | 0.674(7) | 0.234(5) |
| M(3) | 2i | 2.0 | 0.375(1) | 0.949(1) | 0.6165(1) | 0.377(1) | 0.947(1) | 0.616(1) |
| M(4) | 2i | 2.0 | 0.026(1) | 0.199(1) | 0.006(1) | 0.035(2) | 0.205(1) | 0.011(1) |
| V(1) | 2i | 2.0 | 0.8960 | 0.9097 | 0.6673 | 0.8960 | 0.9097 | 0.6673 |
| V(2) | 2i | 2.0 | 0.2221 | 0.6563 | 0.2708 | 0.2221 | 0.6563 | 0.2708 |
| V(3) | 2i | 2.0 | 0.5988 | 0.2685 | 0.1275 | 0.5988 | 0.2685 | 0.1275 |
| O(1) | 2i | 2.0 | 0.072(1) | 0.053(1) | 0.129(1) | 0.071(1) | 0.052(1) | 0.130(1) |
| O(2) | 2i | 2.0 | 0.570(1) | 0.148(1) | 0.223(1) | 0.572(1) | 0.150(1) | 0.223(1) |
| O(3) | 2i | 2.0 | 0.168(1) | 0.437(1) | 0.190(1) | 0.167(1) | 0.434(1) | 0.190(1) |
| O(4) | 2i | 2.0 | 0.976(1) | 0.270(1) | 0.829(1) | 0.976(1) | 0.275(1) | 0.831(1) |
| O(5) | 2i | 2.0 | 0.250(1) | 0.789(1) | 0.962(1) | 0.253(1) | 0.788(1) | 0.966(1) |
| O(6) | 2i | 2.0 | 0.895(2) | 0.966(1) | 0.346(1) | 0.889(2) | 0.966(1) | 0.345(1) |
| O(7) | 2i | 2.0 | 0.550(2) | 0.253(1) | 0.740(1) | 0.540(2) | 0.252(1) | 0.739(1) |
| O(8) | 2i | 2.0 | 0.318(1) | 0.231(1) | 0.964(1) | 0.316(1) | 0.237(1) | 0.965(1) |
| O(9) | 2i | 2.0 | 0.296(1) | –0.005(1) | 0.394(1) | 0.298(1) | –0.002(1) | 0.392(1) |
| O(10) | 2i | 2.0 | 0.216(2) | 0.694(1) | 0.446(1) | 0.215(2) | 0.690(1) | 0.441(1) |
| O(11) | 2i | 2.0 | 0.720(2) | 0.485(2) | 0.256(1) | 0.724(2) | 0.481(1) | 0.254(1) |
| O(12) | 2i | 2.0 | 0.126(2) | 0.299(1) | 0.415(1) | 0.132(2) | 0.303(1) | 0.419(1) |

M(1) = Mn; M(2) = 1.60(2)Mn+0.40(2)Fe; M(3) = 0.08(2)Mn + 1.92(2)Fe; M(4) = 0.32(2)Mn + 1.68(2)Fe

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

The bond lengths and angles for the $Zn_3Fe_4V_6O_{24}$ compound at both investigated temperatures as well as the average values for the system $\beta$-$Cu_3Fe_4V_6O_{24}$ were calculated and compared [11]. The temperature dependences of the metal-oxygen bond lengths in $Mn_3Fe_4V_6O_{24}$ were calculated from the measurements at 290 K and 10 K, and the following values were obtained:

$$\Delta d_{1T} = \langle M(1)–O\rangle_{[4+2]}(290) – \langle M(1)–O\rangle_{[4+2]}(10) = 0.007\ \text{Å}$$

$$\Delta d_{2T} = \langle M(1)\text{–}O\rangle_{[4]}(290) - \langle M(1)\text{–}O\rangle_{[4]}(10) = 0 \text{ Å}$$

$$\Delta d_{3T} = \langle M(2)\text{–}O\rangle(290) - \langle M(2)\text{–}O(10)\rangle = -0.05 \text{ Å}$$

$$\Delta d_{4T} = \langle M(3)\text{–}O\rangle(290) - \langle M(3)\text{–}O\rangle(10) = -0.003 \text{ Å}$$

$$\Delta d_{5T} = \langle M(4)\text{–}O\rangle(290) - \langle M(4)\text{–}O\rangle(10) = 0 \text{ Å}$$

Thermal expansion is dominated by changes in distances involving M(2) positions. Bulk crystal unit cell parameters are changed between 10 K and 290 K in the following way: $\Delta a_T = -0.001$ Å, $\Delta b_T = 0.003$ Å, $\Delta c_T = 0.006$ Å, and the volume change $\Delta V_T = 0.7$ Å$^3$. As can be seen, this thermal expansion is strongly anisotropic, being largest in the *c* direction and smallest in the *a* direction.

This neutron diffraction study of $Mn_3Fe_4V_6O_{24}$ powder has shown that the iron(III) and manganese(II) ions have a disordered structure, and that the distributions on the octahedral and trigonal bipyramidal sites are non-statistical. Some cations are disordered between octahedral iron and fivefold coordinated copper sites, and for the $\beta$-$Cu_3Fe_4V_6O_{24}$ compound this was detected by using Mossbauer spectroscopy [11]. X-ray diffraction analysis of the $Mn_3Fe_4V_6O_{24}$ system has shown that its iron atoms are not disordered with manganese atoms on any sites in this material. This is in contrast to our neutron diffraction study of this compound, because we have found a mixing of Mn and Fe ions at the M(2), M(3), and M(4) sites.

## 4. Conclusions

The $Mn_3Fe_4V_6O_{24}$ compound has been synthesized from MnO, $V_2O_5$, and $Fe_2O_3$. Neutron diffraction measurements were carried out at two selected temperatures – at room temperature and at 10 K. The analysis of the diffraction patterns has not shown any long-range magnetic order, and it produced better crystallographic results than those obtained from XRD analysis for the same system. The value of $\Delta d$ (the difference between Fe(1)–Fe(1) and Fe(2)–Fe(2) distances) is equal to 0.182 Å for the $Mn_3Fe_4V_6O_{24}$ compound, being close to that for the isostructural $\beta$-$Cu_3Fe_4V_6O_{24}$ compound (–0.060 Å). We suggest that the coexistence of two different magnetic ions in these lattices could essentially influence these distances, which is especially evident in the case of the manganese(II) ion, whose magnetic momentum is greater than that of the copper(II) ion. The thermal expansion process in $Mn_3Fe_4V_6O_{24}$ has shown a strongly anisotropic character. The neutron diffraction method, in contrast to XRD, has revealed the existence of manganese and iron ion disorder at M(2), M(3), and M(4) sites in $Mn_3Fe_4V_6O_{24}$.

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