Competition of magnetic interactions in $M_3Fe_4V_6O_{24}$ (M(II) = Zn, Cu, Mn, Mg) compounds studied by EPR

G. Zolnierkiewicz[a], N. Guskos[a,b], J. Typek[a,*], E.A. Anagnostakis[b], A. Blonska-Tabero[c], M. Bosacka[c]

[a] Institute of Physics, Szczecin University of Technology, Al. Piastow 17, 70-310 Szczecin, Poland
[b] Solid State Physics, Department of Physics, University of Athens, Panepistimiopolis, 15 784 Zografos, Athens, Greece
[c] Department of Inorganic and Analytical Chemistry, Szczecin University of Technology, Al. Piastow 17, 70-310 Szczecin, Poland

ABSTRACT

Multicomponent vanadates $M_3Fe_4V_6O_{24}$ (M = Zn(II) and Mn(II)) have been synthesized using the solid-state reaction method from appropriate MO, V_2O_5, and Fe_2O_3 metal oxides. The temperature dependence of the electron paramagnetic resonance (EPR) spectra has been performed in the 90–290 K temperature range. Both the resonance field and the integrated intensity of the EPR spectrum have shown a minimum at ~220 K. Comparison with the results of related study on the $M_3Fe_4V_6O_{24}$ (M = Mg(II) and Cu(II)) compounds has been made. The observed behaviour of the EPR integrated intensity is similar to what is registered for the nanoscale systems of the exchange coupled magnetic ions. The thermal effect of the EPR parameters is more pronounced if two different magnetic ions are present in the same sublattice. The short-range ordered spin clusters interaction and reorientation in the high temperature range could change an effective internal magnetic field which in turn modifies the resonance condition and shifts the observed resonance line. This behaviour could be attributed to the inherent magnetic inhomogeneity of the system (magnetic multiphase) due to the presence of various valence states of the magnetic ions.

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1. Introduction

The compounds in the multicomponent vanadates system M–Fe(Cr)–V–O (M(II) = Zn(II), Mg(II), Ni(II), Cu(II) and Co(II)) are known to display very interesting and complicated physical phenomena [1–10]. The disorder in position of metal ions and the oxygen deficiency processes [4,6,11] could be responsible for the observed magnetic frustration effects [5,8,10]. Additionally, the coexistence of two different, magnetic ions (nickel(II) and iron(III)) could lead to formation of very complicated structural and magnetic states in which the ferroelectric with antiferromagnetic phases could be present [12,13]. In the $Ni_2FeV_3O_{11}$ compound the temperature dependence of dc magnetic susceptibility has shown extraordinary behaviour at temperatures about 200 K connected with magnetic ordering processes [13]. The temperature dependence of the electron paramagnetic resonance (EPR) spectra of $M_3Fe_4V_6O_{24}$ (M = Zn(II) and Cu(II)) has shown the shift of the resonance line and a minimal value of the resonance field was registered at 200 K. In this temperature range the spin system of iron(III) ions attempts to order but the competition of magnetic interactions

prevents it from achieving the magnetic long-range order phase [6,14]. In those compounds belonging to the M–In–V–O system that have two diamagnetic ions in a single sublattice the vanadium ions complexes in lower than nominal oxidation state have been registered [15]. Their presence causes considerable complication of the physical properties of these compounds.

In this work, the temperature dependence of the EPR spectra of recently synthesized vanadates $M_3Fe_4(VO_4)_6$ (M = Zn(II) and Mn(II)) obtained by the solid-state reaction from the MO, V_2O_5, and Fe_2O_3 (M = Zn(II) and Mn(II)) oxides, has been studied. In connection with the previously studied $M_3Fe_4(VO_4)_6$ (Cu(II) and Mg(II)) vanadates, the above system is providing the opportunity to investigate the role of magnetic inhomogeneity produced by two strong magnetic ions. It will be shown that in the multicomponent vanadates system two iron(III) ion sublattices compete in formation of the long-range ordered states leading to the extraordinary behaviour exactly in the same temperature range.

2. Experimental

Polycrystalline samples of the multicomponent vanadates $M_3Fe_4(VO_4)_6$ (M = Zn and Mn) were prepared from the solid-state reaction between 37.50 mol.% MO, 37.50 mol.% V_2O_5 and 25 mol.% Fe_2O_3 [16]. The crystal structure of the $M_3Fe_4(VO_4)_6$ compounds was investigated by the XRD and neutron powder diffraction measurements using the high luminosity DN-2 time-of-flight powder diffractometer on the

* Corresponding author.
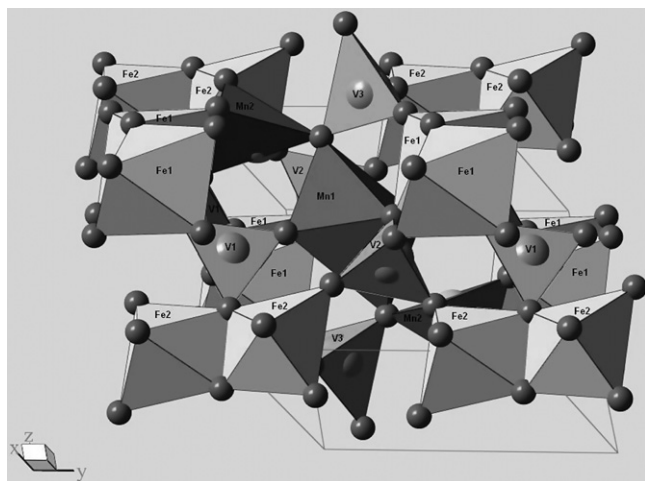E-mail address: typjan@ps.pl (J. Typek).

Fig. 1. The crystal structure of the $Mn_3Fe_4(VO_4)_6$ compound with highlighted metal–oxygen polyhedra.

IBR-2 pulsed reactor [17,18]. The neutron diffraction patterns were collected at 10 K and 290 K to explore the presence of any possible magnetic contribution.

The EPR spectra were recorded using a standard X-band spectrometer Bruker E 500 (ν = 9.46 GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with a NMR magnetometer. The measurements were performed in the temperature range of 90–290 K using an Oxford liquid nitrogen flow cryostat.

3. Results and discussion

$M_3Fe_4(VO_4)_6$ (M = Zn(II), Cu(II), Mg(II) and Mn(II)) system is build up from $M1O_6$ polyhedra, $M2O_5$ trigonal bipyramids, $M3O_6$ and $M4O_6$ octahedra and isolated VO_4 tetrahedra. Fe atoms have been found to occupy exclusively the M3 and M4 sites, while M atoms occupies the M1 and M2 sites [17,18]. Fe_2O_{10} octahedral dimers alternate with MO_5 bipyramids to form edge-sharing chains, while the MO_6 octahedra are located between the chains and share corners with both the MO_5 and Fe_2O_{10} units. Bipyramid MnO_5 is connected with the MnO_6 polyhedron, with one Fe1 octahedral dimer and one Fe2 dimer through the O11 atom, O7–O6 edge and O4–O8 edge, respectively. Fe1 and Fe2 octahedra form edge-sharing dimeric units. The $Fe2_2O_{10}$ octahedral dimers are surrounded by 10 isolated VO_4 tetrahedra, sharing each corner with the Fe2 dimer, and therefore form a $Fe(2)_2V_{10}$ unit. Only eight VO_4 tetrahedra are connected to a $Fe1_2O_{10}$ unit, since two $V2O_4$ share two vertices with the dimer, leading to a $Fe1_2V_8$ unit. Fig. 1 shows the $Mn_3Fe_4(VO_4)_6$ crystal structure, where the Fe dimer network is emphasized, with the Fe2 dimers being those located near the corners of the unit cell. The Fe1–Fe1 and Fe2–Fe2 distances are shown in Table 1 for the four different compounds. The distance Fe1–Fe1 is the greatest for the compound with Mn(II) ions and thus the magnetic dipole–dipole interaction could be the weakest for that compound.

Fig. 2 shows representative EPR spectrum of the $Mn_3Fe_4(VO_4)_6$ compound at 290 K. A single, almost symmetrical, broad resonance line at $g \approx 2.0$ dominates the high temperatures range and the lineshape analysis shows that it can be fit to a single Lorentzian
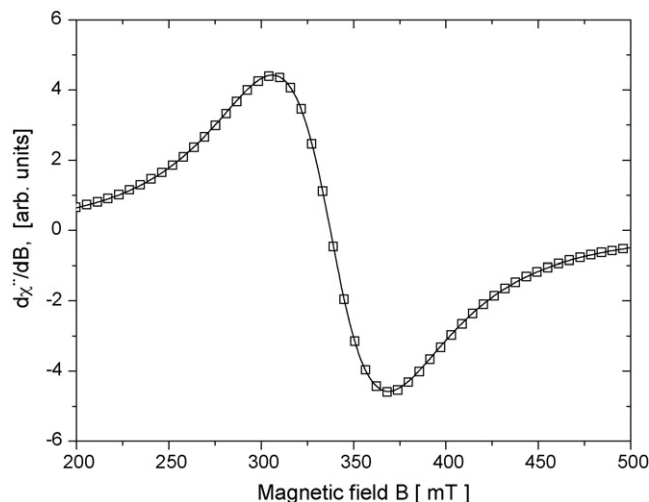

Fig. 2. The EPR spectrum of $Mn_3Fe_4(VO_4)_6$ at 290 K: open squares, experimental points; solid curve, fitting by Lorentzian curve.

line, provided that the contribution of the resonance absorption at negative fields is taken into account. This contribution is due to the linearly polarized microwave field and becomes important when the width of the line becomes comparable to the resonance field. The EPR line broadens continuously as temperature decreases. The linewidth for sample with Mn(II) ions is the smallest and for sample with Mg(II) ions is the greatest (Fig. 3a). From Table 1 it could be seen that the linewidth correlates roughly with the distances d_{11} = Fe1–Fe1 between Fe1 irons ions: the greater the d_{11}, the broader the line. It could be also noticed that the room temperature linewidth of magnetic ions (Mn(II) and Cu(II)) is smaller than for the non-magnetic ions. This could be explained by the narrowing action of the exchange interaction. Comparison of the linewidths of magnetic and non-magnetic ion with a similar d_{11} distance (namely Cu(II) and Mg(II)) allows to estimate the contribution of the exchange interaction at about 30% to the total room temperature linewidth.

Fig. 3b presents the temperature dependence of the EPR integrated intensity for four various compounds differing in type of ions replacing the M(II) cations in $M_3Fe_4(VO_4)_6$. The integrated intensity was calculated as the product of the signal amplitude and the square of the linewidth. For all studied samples the behaviour of the integrated intensity with decreasing temperature is similar and that dependence reaches a minimum at about 220 K. A similar conduct of integrated intensity is observed for the system of magnetic nanoparticles embedded in a non-magnetic matrix [20]. This does not mean that the paramagnetic ions in the investigated multicomponent vanadates form nanoparticles, but only that the mechanisms responsible for the thermal behaviour of certain EPR parameters might be similar. On the other hand magnetic clustering of paramagnetic ions in $M_3Fe_4(VO_4)_6$ compounds is not excluded in view of the presence of different sublattices in that system.

Fig. 3c summarizes the temperature dependence of the resonance field for all four samples. The resonance field shifts with temperature decrease toward the direction of lower magnetic fields

Table 1
Distances (in nm) between iron(III) ions [1,17–19]

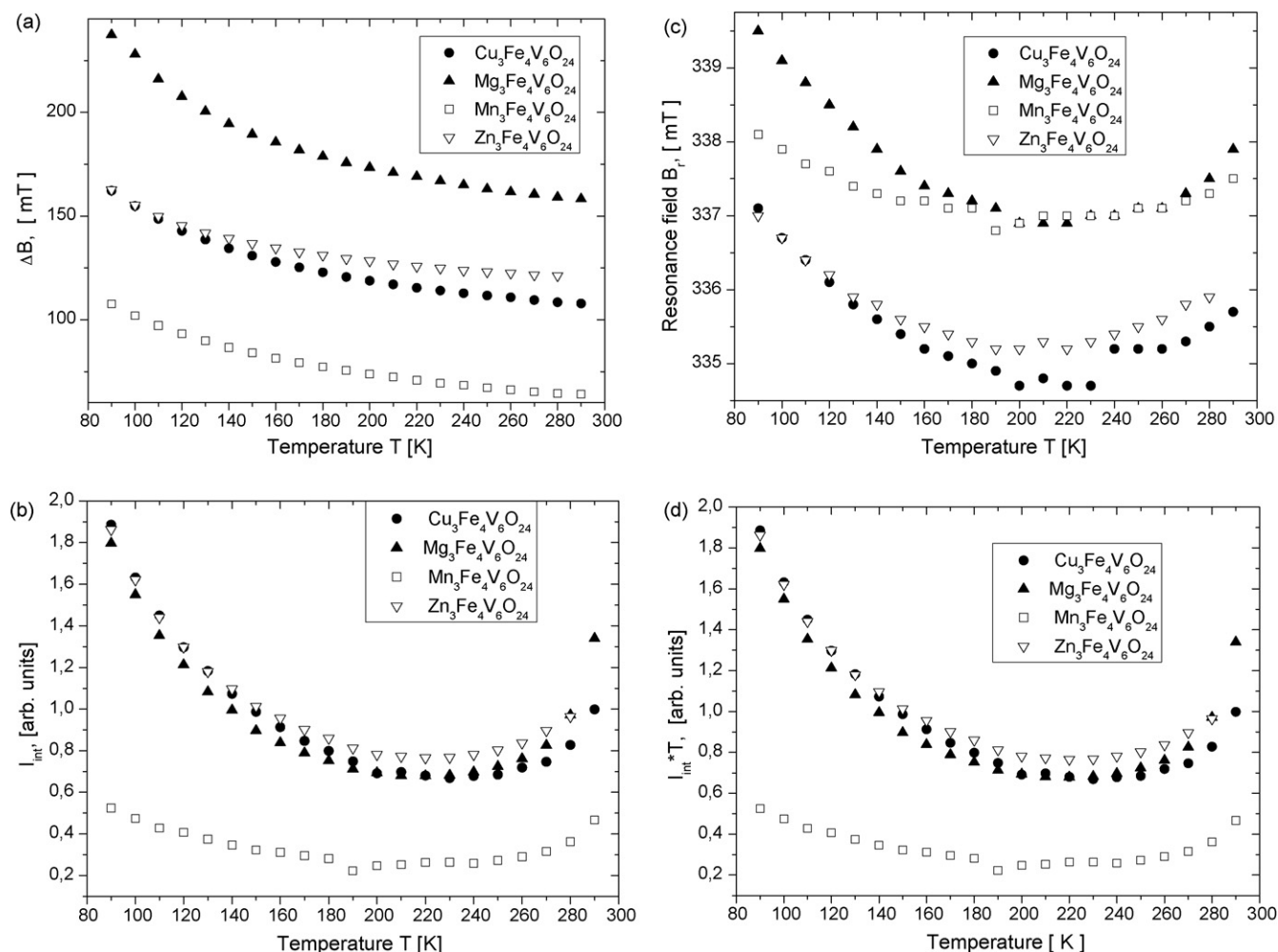|	Compound			
	$Mg_3Fe_4V_6O_{24}$	$Cu_3Fe_4V_6O_{24}$	$Zn_3Fe_4V_6O_{24}$	$Mn_3Fe_4V_6O_{24}$
$d_{11} = d_{Fe1-Fe1}$	0.3066	0.3095	0.3117	0.3347
$d_{22} = d_{Fe2-Fe2}$	0.3193	0.3152	0.3192	0.3153
$\Delta d = d_{11} - d_{22}$	−0.0127	−0.0057	−0.0075	0.0194

Fig. 3. The temperature dependence of the EPR spectral parameters of $M_3Fe_4(VO_4)_6$ (M(II) = Zn(II), Mg(II), Mn(II) and Cu(II)): (a) the linewidth, (b) the EPR integrated intensity, (c) the resonance field, and (d) the product of integrated intensity and temperature.

in temperature above 220 K, and towards higher magnetic fields in temperature below 200 K (Fig. 3b). Table 2 presents the values of temperature gradient of the resonance field $\Delta B_r/\Delta T$ for two regions of temperature. The smallest value of $\Delta B_r/\Delta T$ is recorded for sample with Mn(II) ions.

An interesting relationship could be observed between the values of $\Delta B_r/\Delta T$ gradients and the distances d_{11} for four studied $M_3Fe_4(VO_4)_6$ compounds (Fig. 4a). The $\Delta B_r/\Delta T$ gradients in the 90–150 K range and in the 260–290 K range correlate well with the d_{11} distances. The bigger the d_{11} distance the smaller the modulus of this gradient. A different situation is observed for the Fe2 sublattice. There seems to be no correlation between d_{22} distances and the $\Delta B_r/\Delta T$ gradients (Fig. 4b). The value of the gradient is not dependent on the change of the d_{22} distance. This could indicate on domination in the EPR spectrum of the Fe(III) ions sites in a particular sublattice. There is no visible correlation between the

value of the $\Delta B_r/\Delta T$ gradients and the Fe–O–Fe angles between neighbouring iron(III) ions in Fe1 and Fe2 sublattices.

The dominating magnetic interaction in a specific temperature range could be inferred from the temperature dependence of the product of the integrated intensity and temperature. This product is proportional to the square of an effective magnetic moment (Fig. 3d). Above 180 K the effective magnetic moment decreases with temperature decrease what indicates on domination of the antiferromagnetic interaction. Below 180 K the effective magnetic moment increases with temperature decrease what suggests domination of the ferromagnetic interaction.

The internal magnetic field could modify the magnetic resonance condition [9,14] in the following way: $h\nu = g\,\mu_B\,(B_o - B_{int})$, where h is the Planck constant, μ_B the Bohr magneton, ν the microwave frequency, B_o the external applied magnetic field and B_{int} is the internal magnetic field. If it is supposed that the main part

Table 2
The values of $\Delta B_r/\Delta T$ gradient (in mT/K) for two different temperature ranges [9,14]

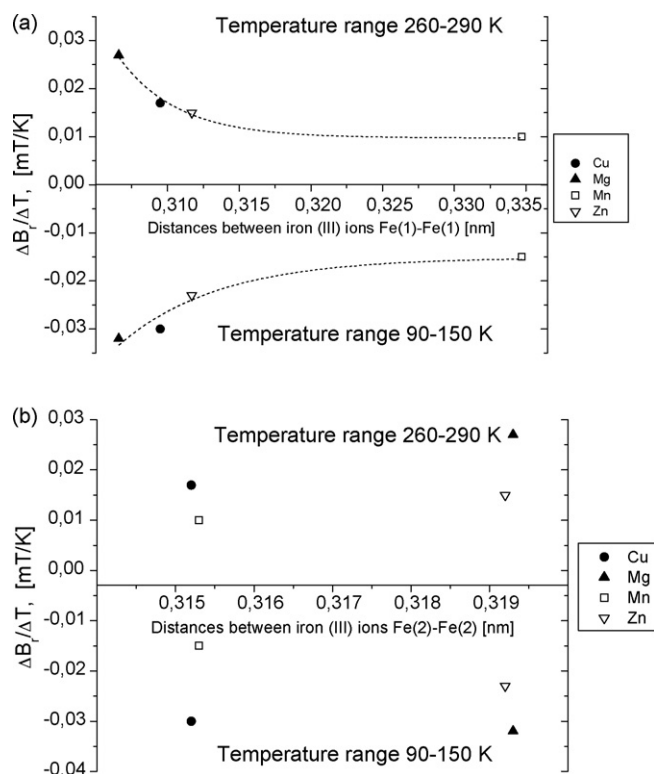|	Compound			
	$Mg_3Fe_4V_6O_{24}$	$Cu_3Fe_4V_6O_{24}$	$Zn_3Fe_4V_6O_{24}$	$Mn_3Fe_4V_6O_{24}$
260–290 K temperature range	0.027	0.017	0.015	0.010
90–150 K temperature range	−0.032	−0.030	−0.023	−0.015
T_{min} (K)	220	230	220	~220

Fig. 4. Dependence of the values of the $\Delta B_r / \Delta T$ gradients on the Fe1–Fe1 distances (a), and Fe2–Fe2 distances (b), for four $M_3Fe_4(VO_4)_6$ compounds.
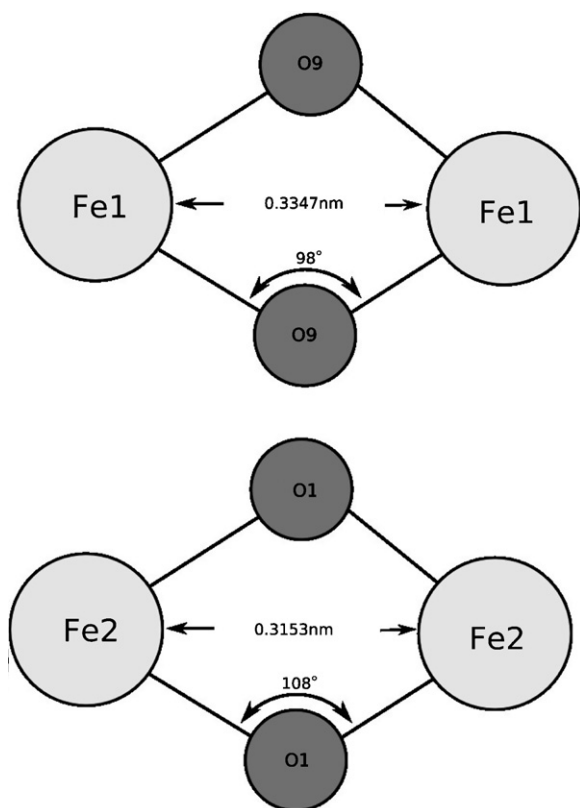
of the internal magnetic field arises from the dipole–dipole interactions the magnetic dipole inside the sample could be subjected to an average magnetic field given by $B_j = \sum[(3\cos^2\theta_i - 1)/r_{ij}^3]\mu_i$, where B_j is an internal magnetic field acting on the jth magnetic center, θ_i the angle of the ith magnetic dipole with the direction of an external magnetic field, r_{ij} the distance between magnetic dipoles, and μ_i is the magnetic moment of the ith dipole. A similar behaviour of the resonance field with temperature was observed for a small amount of magnetic nanoparticles embedded in a non-magnetic polymer matrix. The values of the internal magnetic fields in that case strongly depended on the sizes of magnetic nanoparticle agglomerates [21]. In a system with only one sublattice of Fe(III) ions, e.g. in Fe_2VO_6, an ordered magnetic state was created below 200 K and the observed resonance field shifted to lower values with the temperature decrease, down to very low temperatures [2,22,23]. From the last equation it is seen that when the value of the geometrical factor fulfils the condition $\cos^2\theta > 1/3$, the internal magnetic field is positive, while for $\cos^2\theta < 1/3$ it is negative. If the angle θ for a part of the spin system fulfils the former condition and the other part the later condition, the shift of resonance field would has an opposite direction. That could explain the thermal behaviour of the resonance line, especially for a system with different magnetic sublattices. Calculation of the temperature dependence of resonance field for $M_3Fe_4(VO_4)_6$ compounds using the equation for an internal field B_j is not feasible though because many important parameters (e.g. local thermal expansion coefficient, geometry of the magnetic cluster) are not known. The same phenomenon of geometrical factor change would also account for the competition processes that play a very important role in the frustration phenomena. The competition of magnetic interactions is probably responsible for the lack of magnetically ordered states in the $M_3Fe_4(VO_4)_6$ compounds (Fig. 5).

4. Conclusion

Coexistence of two subsystems of magnetic iron(III) ions in the multicomponent vanadates compounds M–Fe–V–O (M(II) = Zn(II), Mg(II), Cu(II) and Mn(II)) has lead to the competition of magnetic interactions forming a frustrated system that prevented creation of an magnetic ordered state at high temperatures. Additional magnetic ions in $M_3Fe_4(VO_4)_6$ (M = Cu and Mn) compounds have produced an extra magnetic sublattice which has a strongly influence on the above ordering processes. It is very surprising that replacement of different M(II) ions in the multicomponent vanadates system produces such similar behaviour in the high temperature range.

Acknowledgment

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Fig. 5. Schematic diagram presenting distances and angles between neighbouring iron(III) ions in Fe1 and Fe2 sublattices in $Mn_3Fe_4V_6O_{24}$.

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