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High temperature EPR study of the $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg and Mn)

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Electron paramagnetic resonance (EPR) spectra of $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg and Mn) compounds in high temperature range (293 K to 493 K) have been investigated. The role of magnetic (Cu, Mn) and non-magnetic (Zn, Mg) ions in $M_3Fe_4V_6O_{24}$ structure in formation of magnetic resonance spectra was studied. Temperature dependence of EPR parameters: resonance field, linewidth and integrated intensity were examined. Similarities and differences in temperature behavior of these parameters has been discussed in terms of different relaxation mechanisms and magnetic interactions in the spin systems. An important role of additional magnetic ions (M = Mn or Cu) in the $M_3Fe_4V_6O_{24}$ structure has been identified and its consequences considered.

Keywords: *electron paramagnetic resonance; magnetic properties; vanadates*

1. Introduction

The $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg, Mn and Co) compounds have been investigated for some time due to their interesting physical properties and ability to be used in different applications [1–8]. Some of them belong to the howardevansite-group of minerals and recently two new minerals of this type were discovered in volcanic exhalations from the last eruptions of volcanoes in Kamchatka [9]. The crystal structures of $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg and Mn) powders were determined by application of XRD and neutron diffraction methods [1, 3, 10, 11]. The structure contains three sublattices associated with metal ions including two sublattices with iron ions. The M ion site may be occupied by magnetic or diamagnetic ions and in case of the former one a more complex magnetic system is achieved. Measurements of DC magnetic susceptibility χ as a function of

temperature showed that the Curie-Weiss behavior, $\chi = C/(T - \theta)$, dominates at high temperatures with a negative Curie-Weiss temperature θ (the largest value of θ was found for the compound M = Mn and the smallest for M = Cu) [5, 7, 12, 13]. It should be emphasized that introduction of a strong magnetic ion at M site significantly increases the value of θ, while weak magnetic ions, like copper, reduces it. At low temperatures the magnetic frustration processes were observed.

The main electron paramagnetic resonance (EPR) spectrum in all investigated compounds consists of a symmetrical, intense and broad line [4, 6, 7, 14–16]. In addition, the compounds with M = Mn and Cu show the lines derived from the manganese and copper ions with various spin-lattice relaxations [7, 16]. At room temperature, the EPR amplitude is the greatest for the compound M = Mn, while the linewidth of this resonance line is the narrowest [16]. For compounds M = Zn, Mg the resonance line parameters are comparable and the M = Cu compound shows a similar behavior

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to M = Mn sample. Thus it is evident that the relaxation processes significantly depend on the presence of magnetic ions (M = Cu and Mn) and it is seen that the higher the magnetic moment the more intense change of the EPR parameters of that compound. Despite the fact that their crystallographic structures are well known, one of the main problems lies in determination of the magnetic centres that are responsible for the formation of the observed EPR spectra [3, 5, 7, 8, 13]. In [16] it was suggested that there is a strong possibility of the occurrence of magnetic clusters in these compounds. In that case the presence of ferromagnetic resonance (FMR) lines in EPR spectra is not excluded. Under such assumption a lot of differences between the measurements of DC magnetic susceptibility and magnetic resonance could be successfully explained. Besides, in the studied compounds, at a temperature of about 200 K, magnetic competition effects caused by the existence of different magnetic sublattices, were observed [6, 15].

The aim of this work is to analyse the EPR spectra of four $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg and Mn) samples registered at different temperatures in the range of 293 K to 493 K. Each sample contains magnetic Fe ions and additionally two samples contain a second magnetic ion (Cu or Mn). It would be instructive to compare the obtained results and discuss the observed differences in terms of presence of an additional magnetic ion in the crystal structure. This study may allow to determine which magnetic centre is involved in formation of the EPR spectra and help to determine the nature of magnetic interactions between them.

2. Experimental

The method of preparation and chemical characterization of the investigated powder samples was given in previous papers [17, 18]. Furthermore, detailed structural studies have been presented in earlier papers [3, 5, 7, 13]. EPR measurement in the range of 293 K to 493 K were carried out on Radiopan SE/X 2544-M spectrometer equipped with a homemade high-temperature unit.

3. Results and discussion

Fig. 1 shows the EPR spectra of four investigated $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg and Mn) samples registered at different temperatures in the high-temperature range. In the whole studied range of temperatures a symmetric and intense resonance line was observed for all four investigated compounds. The experimental spectra were successfully fitted with Lorentzian lineshape function, similar as it was previously done in the case of lower temperatures [5]. Fig. 2 to Fig. 4 present temperature dependence of the calculated EPR spectra parameters: effective g-factor (g_{eff}), peak-to-peak linewidth (ΔB_{pp}), and the integrated intensity (I_{int}) as well as the inverse of integrated intensity ($1/I_{int}$). The effective g-factor was calculated from the resonance field B_r at the resonance condition ($g_{eff} = \frac{h\vartheta}{\mu_B B_r}$, while the integrated intensity was assumed to be equal to $I_{int} = A \cdot \Delta B_{pp}^2$, where A is the amplitude of EPR signal in the first derivative mode. As the resonance field increases with increasing temperature, the g-factor slightly decreases on heating the samples above ~340 K. For the compounds with magnetic ions at the M (II) site, at temperature of about 450 K, a reverse process is evident. In the range of 340 K to 450 K the shift of the resonance field δB_r (defined as $\delta B_r = B_r(T) - B_r(T + \Delta T)$) shows a nearly linear temperature dependence (Fig. 2). The following values of $\delta B_r/\Delta T$ temperature gradients of that resonance field shift were calculated: $\delta B_r/\Delta T = 7 \times 10^{-3}$ mT/K for $Cu_3Fe_4V_6O_{24}$, $\delta B_r/\Delta T = 6 \times 10^{-3}$ mT/K for $Zn_3Fe_4V_6O_{24}$, $\delta B_r/\Delta T = 6 \times 10^{-3}$ mT/K for $Mg_3Fe_4V_6O_{24}$ and $\delta B_r/\Delta T = 9 \times 10^{-3}$ mT/K for $Mn_3Fe_4V_6O_{24}$. The occurrence of additional magnetic ions (Cu and Mn) in the crystal structure increases the value of that temperature gradient.

Fig. 3 presents temperature dependence of the ΔB_{pp} linewidth. For the two compounds with magnetic ions in the M ion site the linewidth decreases monotonically with increasing temperature, but for $Zn_3Fe_4V_6O_{24}$ and $Mg_3Fe_4V_6O_{24}$ at about 400 K an increase of the linewidth with temperature increase is observed. Closer examination of Fig. 3 shows that three questions should be answered consistently: (a) why the linewidth decreases

with temperature increase for all investigated samples below 400 K, (b) why the linewidth is smaller for the compounds with additional magnetic ions (M = Cu and Mn); (c) why the increase of the linewidth above 400 K is observed only for M = Zn and Mg compounds? A decrease of linewidth with temperature increase is a well-known effect. It was observed for many substances and most often it is explained by invoking the temperature-dependent exchange narrowed spin-spin interaction [19, 20]. A more detail discussion of the role of the exchange narrowing mechanism will be presented later.
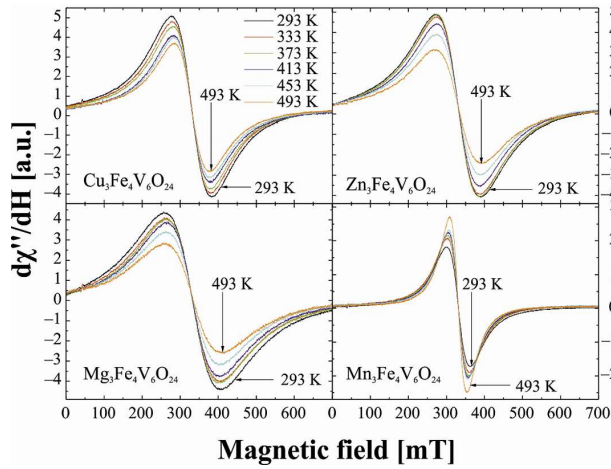

Fig. 1. EPR spectra of investigated $M_3Fe_4V_6O_{24}$ compounds registered at different temperatures.

Fig. 2. Temperature dependence of g_{eff}-factor in $M_3Fe_4V_6O_{24}$ compounds. Standard uncertainties in g_{eff}-factor values are smaller than the sizes of the points. Dotted lines are just guides to the eyes.

Fig. 3. Temperature dependence of the linewidth ΔB_{pp} in $M_3Fe_4V_6O_{24}$ compounds. Standard uncertainties in ΔB_{pp} values are smaller than the sizes of the points. Dotted lines are just guides to the eyes.

In Fig. 4 the temperature dependence of the EPR integrated intensity (I_{int}) and the reciprocal of integrated intensity ($1/I_{int}$) are presented. The EPR integrated intensity is proportional to the magnetic susceptibility of the spin system under study at microwave frequency. The EPR integrated intensity behaves according to Curie-Weiss law, $I_{int} = C/(T - \theta)$, in the temperature range of 333 K to 433 K, where the constant C is related to an effective magnetic moment and the Curie-Weiss temperature θ is positive for ferromagnetic interaction and negative for antiferromagnetic interaction between the involved spins. The following values of θ were calculated: 56(15) K for Cu, 48(4) K for Zn, 17(11) K for Mg, and –170(30) K for Mn compounds. It is expected that the strongest interactions will be found in $Cu_3Fe_4V_6O_{24}$ and $Mn_3Fe_4V_6O_{24}$
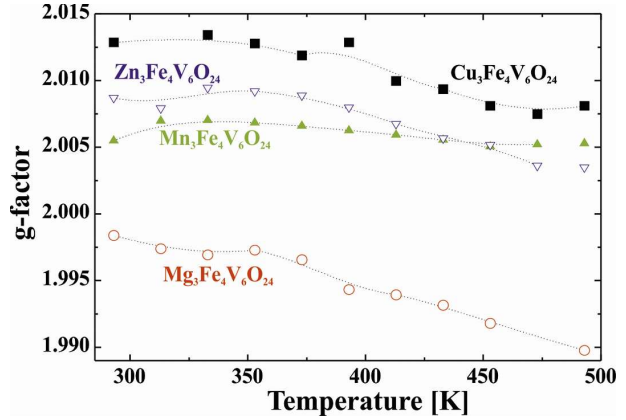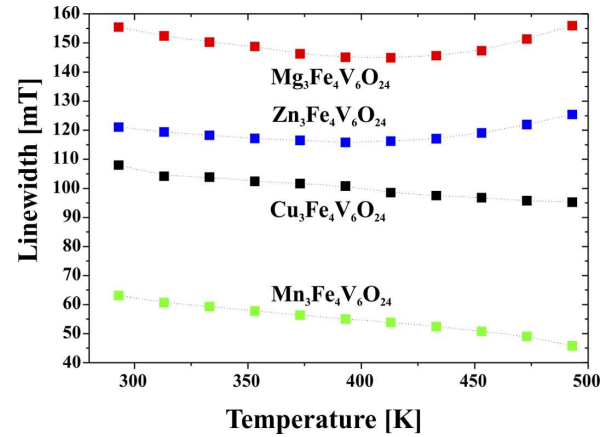
compounds where two different magnetic ions are present in the crystal structure. It is interesting to note that the sign of θ may change going from low (below RT) to high temperatures. As the value of the Curie-Weiss temperature is an indication of an effective interaction strength and interaction type, the change of its sign can be understood as the change of the leading interaction type (antiferromagnetic ↔ ferromagnetic). For $M_3Fe_4V_6O_{24}$ compounds their crystal structures
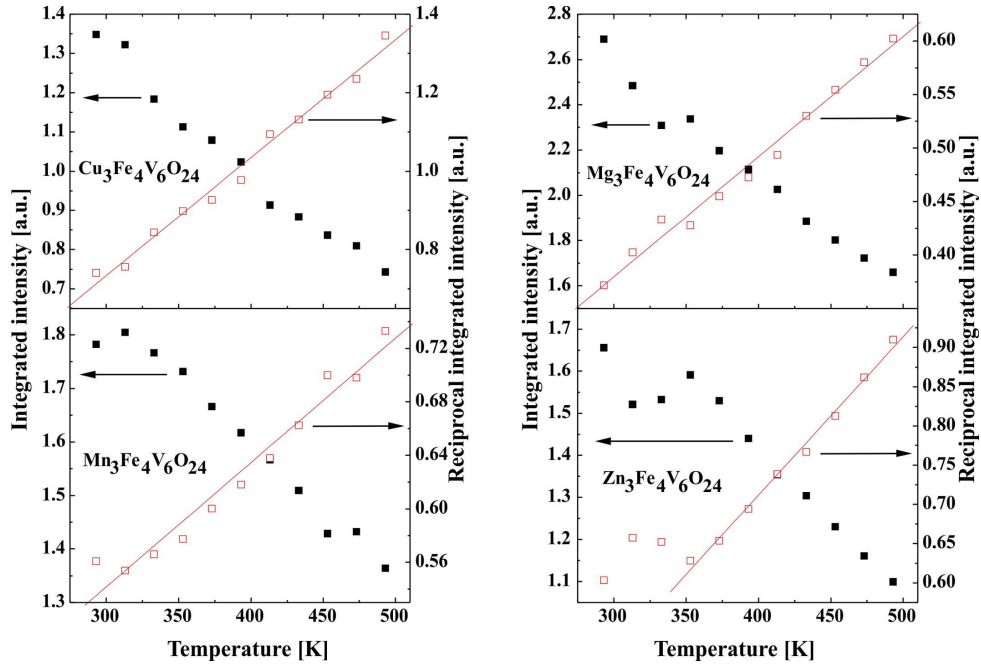
Fig. 4. Temperature dependence of the integrated intensity I_{int} (left axis) and reciprocal integrated intensity (right axis) in $M_3Fe_4V_6O_{24}$ compounds. Standard uncertainties in I_{int} values are smaller than the sizes of the points. The solid lines are the least-squares fits to the experimental points.

contain a few different magnetic sublattices having different types of magnetic interactions and if their strength depends on temperature it could lead to the observed effect of sign change of θ close to RT.

In Fig. 5 the relation between the Curie-Weiss constant C and Curie-Weiss temperature θ is shown. Remarkably, an effective magnetic moment of $Cu_3Fe_4V_6O_{24}$ and $Mn_3Fe_4V_6O_{24}$ compounds is smaller than that obtained for $Zn_3Fe_4V_6O_{24}$ and $Mg_3Fe_4V_6O_{24}$ which indicates the existence of antiferromagnetic interaction between Fe and Cu/Mn ions. This interaction must be especially strong in $Mn_3Fe_4V_6O_{24}$ compound and it overcomes the weaker ferromagnetic interaction in Fe sublattice, causing an overall effective interaction to be antiferromagnetic, as evidenced by the negative sign of the Curie-Weiss temperature. The clustering of magnetic ions, leading to the magnetic frustration at low temperatures, is not excluded in case of $Cu_3Fe_4V_6O_{24}$ and $Mn_3Fe_4V_6O_{24}$ compounds.

It is well known that when the narrowing of the resonance line is produced by temperature dependent exchange interaction, the lineshape is
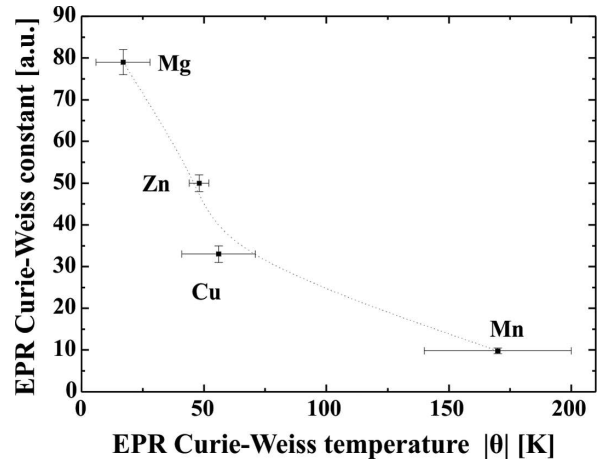

Fig. 5. Dependence of the Curie constant C on the Curie-Weiss temperature θ for all investigated samples. Dotted line is just a guide to the eyes.

Lorentzian. This is also the case for all our EPR spectra. As the exchange-narrowing spin-spin interaction among Fe ions is operating in all four studied compounds, it explains the line narrowing observed there below 400 K. The exchanged-narrow linewidth is usually calculated from

the following equation: $\Delta B = \Delta B_{dip}^2 / B_{ex}$, where ΔB_{dip} is the dipolar linewidth determined by dipol-dipol interaction experienced by each spin from all its neighbouring spins, and B_{ex} is the exchange field which is temperature dependent [20]. As B_{ex} is proportional to the Curie-Weiss temperature, $B_{ex} \sim \theta$, it follows that the exchange narrowed linewidth will be inversely proportional to θ. This explains why the observed linewidths of our four samples at temperatures lower than 400 K are ordered in that particular manner: in the samples with two different magnetic ions we have stronger magnetic interactions and thus narrower EPR lines than in the compounds with only Fe magnetic ions.

In $Zn_3Fe_4V_6O_{24}$ and $Mg_3Fe_4V_6O_{24}$ compounds yet another dynamic relaxation process operates above 400 K (Fig. 3). In consequence, in both the samples the linewidth starts to increase as temperature increases. In general, an increase of linewidth (linear) with temperature increase can be a result of three mechanisms: a direct spin-phonon process (modulation of the crystalline electric field by lattice vibration involving one phonon in the relaxation process), modulation of static Dzyaloshinsky-Moriya interaction between a pair of magnetic ions by a single phonon, and the bottleneck scenario involving relaxation of localized magnetic moments to the lattice via the highly mobile electron system in the metallic regime [21]. It seems very probable that the first mechanism operates in our two Zn and Mg compounds as the second mechanism is usually realized in spin system S = 1/2, while the third mechanism requires no significant shift of the g-factor, contrary to what is observed in our samples (Fig. 2). This spin-lattice mechanism is either suppressed or moved to much higher temperatures in $Mn_3Fe_4V_6O_{24}$ and $Cu_3Fe_4V_6O_{24}$ compounds by the presence of additional magnetic ions that magnify the exchange narrowing processes by increasing and frustrating exchange interactions between magnetic ions.

4. Conclusions

EPR spectra of four compounds $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg, and Mn) have been studied in the high temperature range. Temperature dependence of the resonance field, linewidth and integrated intensities of the observed single and intense Lorentzian line has been determined. At temperatures T < 400 K the observed line is narrowed in all studied compounds and the effect is much larger in $Mn_3Fe_4V_6O_{24}$ and $Cu_3Fe_4V_6O_{24}$ compounds where an additional magnetic ion is placed at the M site. The presence of two different magnetic ions in $M_3Fe_4V_6O_{24}$ structure can be invoked also from temperature dependence of the resonance field and the integrated intensity. In consequence, more complicated magnetic structure of $Mn_3Fe_4V_6O_{24}$ and $Cu_3Fe_4V_6O_{24}$ as compared to $Mg_3Fe_4V_6O_{24}$ and $Zn_3Fe_4V_6O_{24}$ compounds leads to the competition of ferromagnetic and antiferromagnetic interactions and appearance of associated with them magnetic frustration effects.

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