

MAGNETIC RESONANCE STUDY OF $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$

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Received: December 10, 2009

Abstract. The recently discovered multicomponent vanadate $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$, isostructural with the previously studied $\text{Mg}_3\text{Fe}_4(\text{VO}_4)_6$, was synthesized and investigated by the electron paramagnetic resonance (EPR) technique. According to the nominal stoichiometry of the $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ compound the ions (excluding iron ions) are nonmagnetic. The registered EPR spectra in the 4-300K temperature range were dominated by the presence of a very broad almost symmetrical resonance line which disappeared below 20K. At room temperature this resonance line was centred at $H_r=3358$ Gs with linewidth $\Delta H_{pp}=835$ Gs. Its amplitude decreased with the decreasing temperature and below 60K the linewidth strongly depended on the temperature. Below 60K the line shifted significantly with the decreasing temperature towards lower magnetic fields. In the same temperature range the EPR spectra were deconvoluted on two component Lorentzian lines, attributed to two different types of spin clusters. As the ground state of both antiferromagnetic spin clusters was nonmagnetic, the lines were not observed below 20K. The cluster visible in a wide temperature range up to room temperature was attributed to Fe^{3+} spins, while the other cluster observed only at low temperature involved also Cd^{2+} ions.

1. INTRODUCTION

Cadmium is a very interesting element which could cause appearance of electric conductivity when doped at a very low concentration into electrical isolators (with the energy gap over 7.6 eV) [1-3]. It would be very interesting to investigate compounds containing cadmium ions, especially multicomponent vanadates belonging to the M-Fe-V-O system (M - metal ion). The reaction products of FeVO_4 with $\text{M}_2\text{V}_2\text{O}_7$ and FeVO_4 with $\text{M}_3\text{V}_2\text{O}_8$ could be the multicomponent vanadates $\text{M}_2\text{FeV}_3\text{O}_{11}$ and $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ (where M = Zn, Mg) possessing different magnetic sublattices [4-7]. Very significant phenomena of magnetic frustration and competition are observed in these materials and intensely studied [8-10]. The introduction of cadmium ions at the site of M(II) cations in multicomponent vanadates could facilitate

the formation of compounds with novel physical properties that might allow better understanding of the magnetic interactions responsible for the frustration and competition processes. Recently, an attempt to synthesize a new multicomponent vanadate by replacing M(II) cations with divalent cadmium has been made [11]. It is known that Cd^{2+} ions can increase the o-semiquinone free radicals concentration in both natural and synthetic melanins [12]. Diamagnetic Cd^{2+} ions increase the concentration of free radicals. These ions may also fasten the spin relaxation processes. Stronger dipolar interactions between paramagnetic centres exist in complexes with Cd^{2+} than in crude ones [12]. The $\text{Cd}_2\text{FeV}_3\text{O}_{11}$ or $\text{Cd}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ compounds in the $\text{CdO}-\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3$ system were not formed, but a new phase $\text{Cd}_4\text{Fe}_7+x\text{V}_9+x\text{O}_{37}+4x$ ($-0.5 < x < 1.5$) could be synthe-

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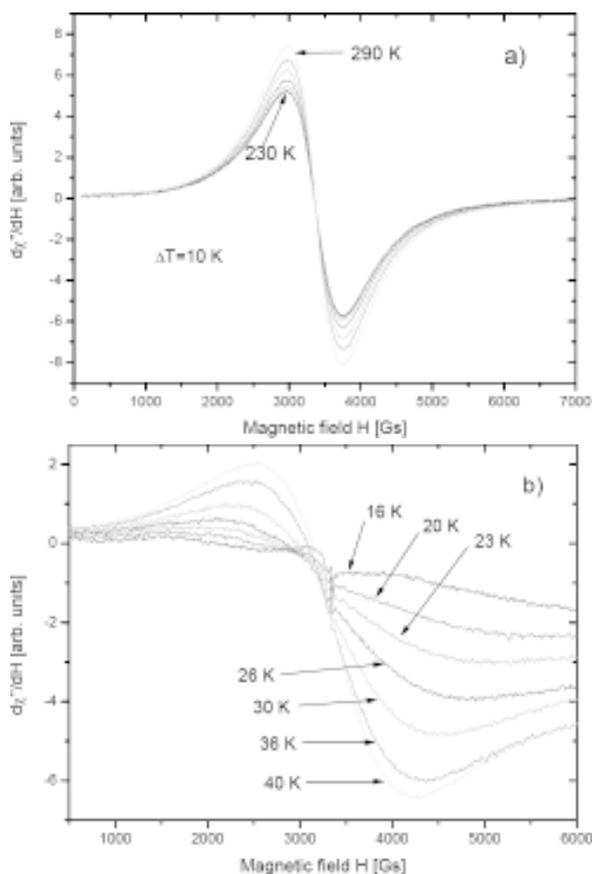


Fig. 1. EPR spectra of the $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ compound registered at different temperatures: high temperature range, $T \geq 230\text{K}$ (a); low temperature range, $T \leq 40\text{K}$ (b).

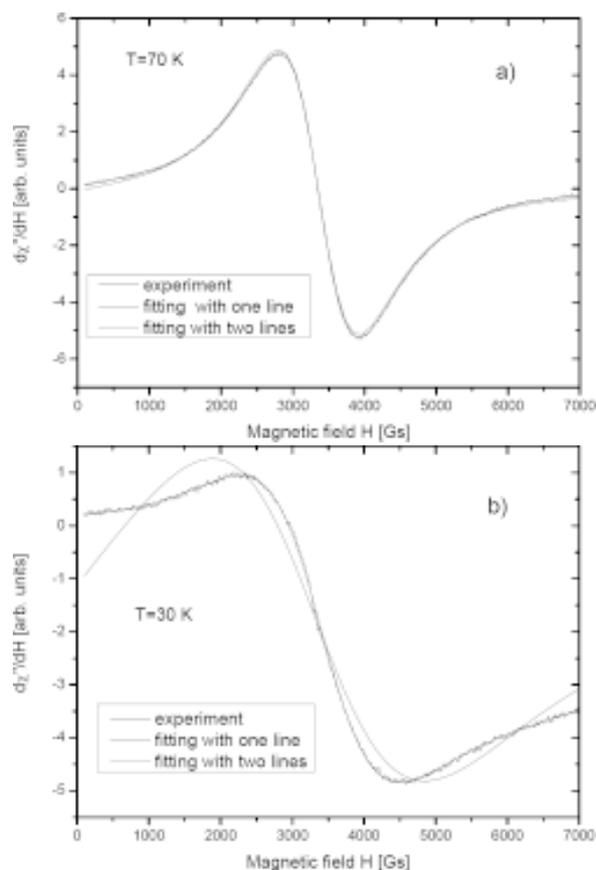


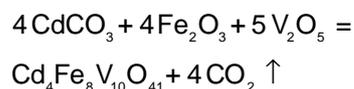
Fig. 2. Comparison of the experimental (black) and fitted lines (blue and red) at $T=60\text{K}$ (a) and $T=30\text{K}$ (b). The fitting was done using one Lorentzian line (blue) and the sum of two different Lorentzian lines (red).

sized. Its melting point decreases from $790(5)^\circ\text{C}$ to $770(5)^\circ\text{C}$ with a decrease in the concentration of cadmium(II) ions.

The aim of this report is to study the temperature dependence of the EPR (electron paramagnetic resonance) spectra of a new multicomponent vanadate $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$. The thermal dependence of magnetic resonance parameters would allow the magnetic properties of this compound to be investigated and a comparison with the previously studied compounds in the M-Fe-V-O system to be made.

2. EXPERIMENTAL

Polycrystalline multicomponent vanadate of $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ was obtained from a solid-state reaction between CdCO_3 , Fe_2O_3 , and V_2O_5 with the following thermal stages: $600^\circ\text{C}(20\text{h}) + 710^\circ\text{C}(20\text{h})$, according to the equation [11]:



The crystal structure of the $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ could be satisfactorily described as a homeotype of $\beta\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [4,11]. The $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ compound crystallized in the triclinic system and the parameters of the unit cell were the following: $a = 0.6734(2)$ nm, $b = 0.8323(3)$ nm, $c = 0.9880(4)$ nm, $\alpha = 106.29(6)$, $\beta = 105.69(5)$, $\gamma = 103.06(5)$ [11].

The EPR spectra were recorded using a standard X-band spectrometer Bruker E 500 ($\nu = 9.455$ GHz) with the magnetic field modulation of 100 kHz. The magnetic field was scaled with a NMR magnetometer. The samples, containing about 30 mg of $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ in form of fine powder were sealed into quartz tubes 4 mm in diameter. The measurements were performed in the 4 to 290K range using an Oxford nitrogen flow cryostat.

3. RESULTS AND DISCUSSION

Fig. 1 presents the EPR spectra of a $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ powder sample taken at different temperatures. An

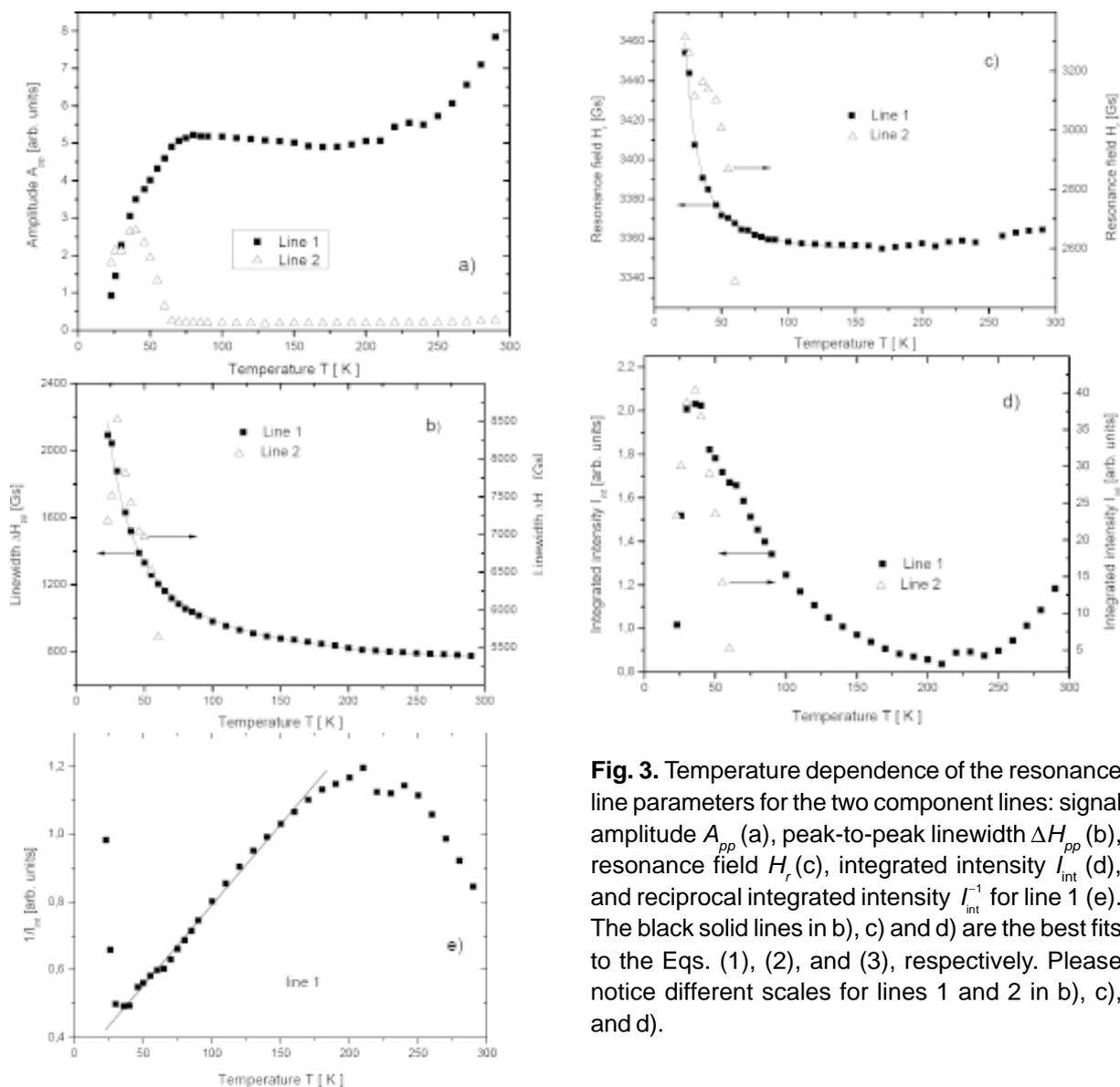


Fig. 3. Temperature dependence of the resonance line parameters for the two component lines: signal amplitude A_{pp} (a), peak-to-peak linewidth ΔH_{pp} (b), resonance field H_r (c), integrated intensity I_{int} (d), and reciprocal integrated intensity I_{int}^{-1} for line 1 (e). The black solid lines in b), c) and d) are the best fits to the Eqs. (1), (2), and (3), respectively. Please notice different scales for lines 1 and 2 in b), c), and d).

almost symmetrical resonance line is observed at high temperatures (Fig. 1a). The registered EPR line at room temperature is centred at $g_{eff}=2.0007(3)$ (resonance field $H_r=3358(1)$ Gs) with the peak-to-peak linewidth $\Delta H_{pp}=835(1)$ Gs. As the temperature decreases the line amplitude decreases and the linewidth slowly increases. Below 60K the line becomes asymmetrical and a strong shift of the resonance field H_r is observed (Fig. 1b). To properly describe the registered derivative spectrum, it was fitted to one or two Lorentzian lines comprising also the resonance absorption tail at negative fields. It is a consequence of a linearly polarized microwave

field that becomes important when the EPR line width becomes comparable to the resonance field, as in the present case. It was noticed that only one Lorentzian line was sufficient for satisfactory fitting of the experimental spectrum for the EPR spectra registered at temperature above 60K (Fig. 2a). This line will be further referred to as line 1. In the low temperature range ($T<60$ K) an additional line (designated as line 2) has to be used for adequate fitting (Fig. 2b). The presence of isolated Fe^{3+} ions in the high spin d5 state (${}^6S_{7/2}$ ground state) was not recorded in EPR spectra in the whole studied temperature range.

Table 1. Resonance field H_r , peak-to-peak linewidth ΔH_{pp} at room temperature and the temperature gradient of resonance field $\Delta H/\Delta T$ in the indicated temperature range for various compounds in the M-Fe-V-O system.

Compound	H_r [Gs]	ΔH_{pp} [Gs]	$\Delta H_r/\Delta T(290-240K)$ [Gs/K]	$\Delta H_r/\Delta T(40-20K)$ [Gs/K]
$Zn_3Fe_4V_6O_{24}$ [18]	3361(1)	1207(1)	0.11	-30.0
$Mg_3Fe_4V_6O_{24}$ [9]	3375(1)	1571(1)	0.08	-28.0
$Mn_3Fe_4V_6O_{24}$ [17]	3375(1)	637(1)	0.11	-20.0
$Cu_3Fe_4V_6O_{24}$ [10]	3357(1)	1072(1)	0.17	
$Cd_4Fe_8V_{10}O_{41}$	3358(1)	835(1)	0.16 (line 1)	-6.0 (line 1)

For the description of EPR spectra of $Cd_4Fe_8V_{10}O_{41}$, the following spectral parameters were calculated by fitting the experimental spectrum with two Lorentzian lines: signal peak-to-peak amplitude A_{pp} , the resonance field H_r , peak-to-peak linewidth ΔH_{pp} , and the integrated intensity I_{int} . The EPR integrated intensity, defined as the area under the absorption resonance curve, was proportional to the imaginary part of the complex magnetic susceptibility. Fig. 3 shows the temperature dependence of these calculated parameters. All parameters depend strongly on temperature.

Fig. 3 presents the temperature dependence of the calculated spectral parameters for both components of the observed EPR spectrum. In Fig. 3a the temperature changes of amplitudes A_{pp} of line 1 and line 2 are illustrated. As can be easily observed the amplitude of line 2 has a meaningful contribution to the observed spectrum only at a low temperature ($T < 60K$) and it could be discarded without any deterioration of the resultant fitting function in the high temperature range. The amplitude of line 1 basically decreases with a temperature decrease except in the 80-220K range where it is nearly constant. The thermal amplitude gradient, $\Delta A_{pp}/\Delta T$, is approximately three times greater in the low temperature range (20-40K) than in the high temperature range (240-290K) (Fig. 3a). A very small value of $\Delta A_{pp}/\Delta T$ in the intermediate temperature range could be explained by assuming the action of a "blocking" process, similar to what is observed in a magnetic nanoparticles system. The spin clusters believed to be present in $Cd_4Fe_8V_{10}O_{41}$ are playing the role of nanoparticles. Other manifestations of spin clusters in this compound will be discussed further. In contrast to line 1, the amplitude of line 2 increases in the 60-40K range with a temperature decrease but quickly decreases on cooling below 40K.

In Fig. 3b the temperature dependence of the peak-to-peak linewidth for both lines is presented. For line designated as 1, the linewidth increases with a temperature decrease and the rate of change is considerable at low temperatures. Such a temperature variation of linewidth ΔH_{pp} is frequently observed near magnetic phase transitions for ordinary antiferromagnets [13] or spin-glasses [14], due to the slowing down of spin fluctuations and the growth of internal fields. If the thermal linewidth change is attributed to the spin-glass to paramagnetic transition at temperature T_f , the following expression could be used [15]

$$\Delta H_{pp} = \Delta H_0 + A \left(\frac{T_f}{T - T_f} \right), \quad (1)$$

where ΔH_0 is the temperature independent linewidth part, and A is a constant. The best fit to the experimental points was obtained for $\Delta H_{pp}(\infty) = 652(10)$ Gs, and $T_f = 0.9(8)K$. The best fit line is presented as a black solid line in Fig. 3b. As far as line 2 is concerned, its linewidth shows some very interesting behaviour – it reaches a maximum at $T = 30K$ and narrows on further cooling.

In Fig. 3c the temperature variations of the resonance field of both lines are presented. At room temperature the resonance field is almost similar to that registered for the $Zn_3Fe_4V_6O_{24}$ compound (Table 1). The resonance field for line 1 increases with the temperature decrease and that change is especially strong at low temperatures. This increase could be attributed to the appearance of local fields created by antiferromagnetically correlated spins. These fields add to the applied external field, changing the resonance condition. Assuming that there are antiferromagnetically correlated spins between ferromagnetic layers, the effective resonance field B_r could be approximated by the equation [16]:

$$H_r(T) = H_0 + \frac{C_1}{T \cdot \exp(C_2/T)}, \quad (2)$$

where C_1 , C_2 , and H_0 are constants and C_2 contains, inter alia, the antiferromagnetic exchange coupling between layers of spins. The best fit to the experimental points (below 150K) was obtained for $H_0 = 3350(2)$ Gs, $C_1 = 640(110)$ Gs·K, $C_2 = -31(4)$ K. The solid line in Fig. 3c shows the dependence given by Eq. (2). A comparison of the temperature gradients of the resonance field $\Delta H/\Delta T$ for various compounds in M-Fe-V-O system (see Table 1) shows that the $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ compound is significantly different in the low temperature range. This dissimilarity could be explained as a result of the presence of an additional paramagnetic centre (responsible for line 2) not found in other compounds. The resonance field of line 2 is basically smaller compared to the resonance field of line 1 and its temperature dependence is quite complicated. In general, the line 2 shifts toward higher magnetic field on cooling, but a local maximum in $H_r(T)$ is observed at $T = 35$ K.

Fig. 3d presents the temperature dependence of the integrated intensity $I_{\text{int}}(T)$ for both component lines. At high temperature I_{int} slowly decreases with the decreasing temperature for line 1 (as was observed for other compounds in Table 1) but below 200K an increase in I_{int} is registered on cooling. In the 40-150K range the temperature dependence of the integrated intensity for line 1 seems to follow the Curie-Weiss law. To obtain the value of Curie-Weiss constant the plot of reciprocal integrated intensity vs temperature was prepared (Fig. 3e). The best fit of the following equation

$$I_{\text{int}}^{-1} = \left(\frac{C_4}{T - T_{\text{CW}}} \right)^{-1} \quad (3)$$

to the experimental points allowed $T_{\text{CW}} = -66(4)$ K to be calculated. The negative sign and a large value of T_{CW} indicate a strong antiferromagnetic interaction between the paramagnetic centres responsible for line 2. It could be noticed that a smaller value of $T_{\text{CW}} = -26$ K has been calculated for a similar $\text{Zn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ compound [18], indicating a weaker antiferromagnetic interaction. As could be seen in Fig. 3d I_{int} reaches a maximum at 40K for both lines and quickly decreases on further cooling. This rapid decrease in intensity in the low temperature range could be explained by assuming a nonmagnetic ground state for both centres. Thus, the thermal behaviour of integrated intensity suggests that magnetic spin clusters of large sizes are formed in $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ [19].

Taking into account all the experimental findings concerning the thermal behaviour of EPR parameters of both lines the following picture emerges that explains consistently the observed changes in the EPR spectrum of the $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ compound. The two component lines are produced by iron spin clusters having a nonmagnetic ground state (antiferromagnetic spin cluster). As in a similar $\text{Zn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ compound only one line was sufficient for fitting the EPR spectra in the whole temperature range it could be deduced that Cd^{2+} ions were involved in formation of the cluster responsible for line 2. This particular spin cluster was only observed at low temperatures, probably due to a very strong coupling to the lattice. On the other hand, the spin cluster responsible for line 1 should be relatively isolated from the surroundings. Hence, intricate competing magnetic interactions in a complicated crystal structure of $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ prevent formation of a global antiferromagnetic state and favour formation of spin clusters.

4. CONCLUSIONS

The recent EPR study of a polycrystalline multi-component vanadate $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ has shown that the temperature dependence of spectral parameters has a similar character to that observed previously for $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ (M(II) = Mg(II), Zn(II), Mn(II), and Cu(II)) system only in the high temperature range, but differs significantly at low temperatures ($T < 60$ K). The presence of an additional paramagnetic centre has to be invoked to adequately describe the low temperature spectrum of $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$. The EPR spectrum has been deconvoluted on two component lines (line 1 and line 2) that are due to two different types of the antiferromagnetic spin clusters. The spin cluster attributed to line 2, visible only at low temperatures, involves both iron and cadmium ions while the spin cluster attributed to line 1 contains only iron ions. A competition of the magnetic interaction prevents formation of an antiferromagnetic phase at high temperatures and the appearance of a spin-glass state ($T_f \approx 1$ K) could be inferred from the temperature dependence the linewidth of line 1.

ACKNOWLEDGEMENT

This scientific work was financed from the Polish budget resources allocated to science in the years 2005-2008 as a research project (1311/TO9/2005/29).

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