



Magnetic resonance study of $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ compound



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Abstract

A new multicomponent vanadate $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ has been synthesized and investigated by electron paramagnetic resonance/ferromagnetic resonance (EPR/FMR) technique. The compound $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ is isostructural with previously studied $\text{Mg}_3\text{Fe}_4(\text{VO})_6$. According to the nominal stoichiometry of the $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ compound the ions (excepted iron ions) are nonmagnetic. The registered EPR spectra in the 4-300 K temperature range have been dominated by the presence of a very broad almost symmetrical resonance line which disappears below 20 K. This resonance line is centred at $g_{\text{eff}}=2.017(1)$ with linewidth $\Delta H_{\text{pp}}=835$ Gs at room temperature. Its amplitude decreases with decreasing temperature and below 70 K the linewidth strongly depends on temperature. Below 60 K the line shifts significantly with decreasing temperature towards lower magnetic fields. It is suggested that the presence of strong magnetic interaction leads to magnetically ordered state. Replacement of non-magnetic cations by divalent cadmium ions seems to intensify the magnetic ordering processes at low temperatures.

Introduction

Cadmium is a very attractive element that doped at very low concentration into electrical isolators (with energy gap over 7.6 eV) could cause appearance of electric conductivity [1-3]. It would be very interesting to investigate compounds contain 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 $\text{M}_3\text{V}_5\text{O}_{14}$ 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]. Much studied and very remarkable phenomena of magnetic frustration and competition are observed in these materials [8-10]. The introduction of cadmium ions at the position of cations M(II) in multicomponent vanadates could facilitate formation of compounds with novel physical properties that might allow better understanding 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 was made [11]. In the $\text{CdO}-\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3$ system the $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ or $\text{Cd}_4\text{Fe}_8\text{V}_x\text{O}_{37+4x}$ ($-0.5 < x < 1.5$) could be synthesized. Its melting point decreasing from 790(5)°C to 775(5)°C with concentration decrease of cadmium(II) ions.

The aim of this report is to study the temperature dependence of the EPR/FMR (electron paramagnetic resonance/ferromagnetic 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 investigating the magnetic properties of this compound and making comparison with previously studied compounds from the M-Fe-V-O system.

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 $5\text{V}_2\text{O}_5$ with the following thermal stages: 600 °C(20h) + 710 °C(20h), 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 $\beta\text{-Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [1]. The $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ compound crystallizes in the triclinic system and the parameters of the unit cell are the following: $a=0.6734(2)$ nm, $b=0.8323(3)$ nm, $c=0.9880(4)$ nm, $\alpha=106.29(6)^\circ$, $\beta=105.69(5)^\circ$, $\gamma=103.06(5)^\circ$. The EPR/FMR spectra were recorded using a standard X-band spectrometer Bruker E 500 (9.455 GHz) with 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 4 mm in diameter quartz tubes. The measurements were performed in 4 to 290 K temperature range using an Oxford helium flow cryostat.

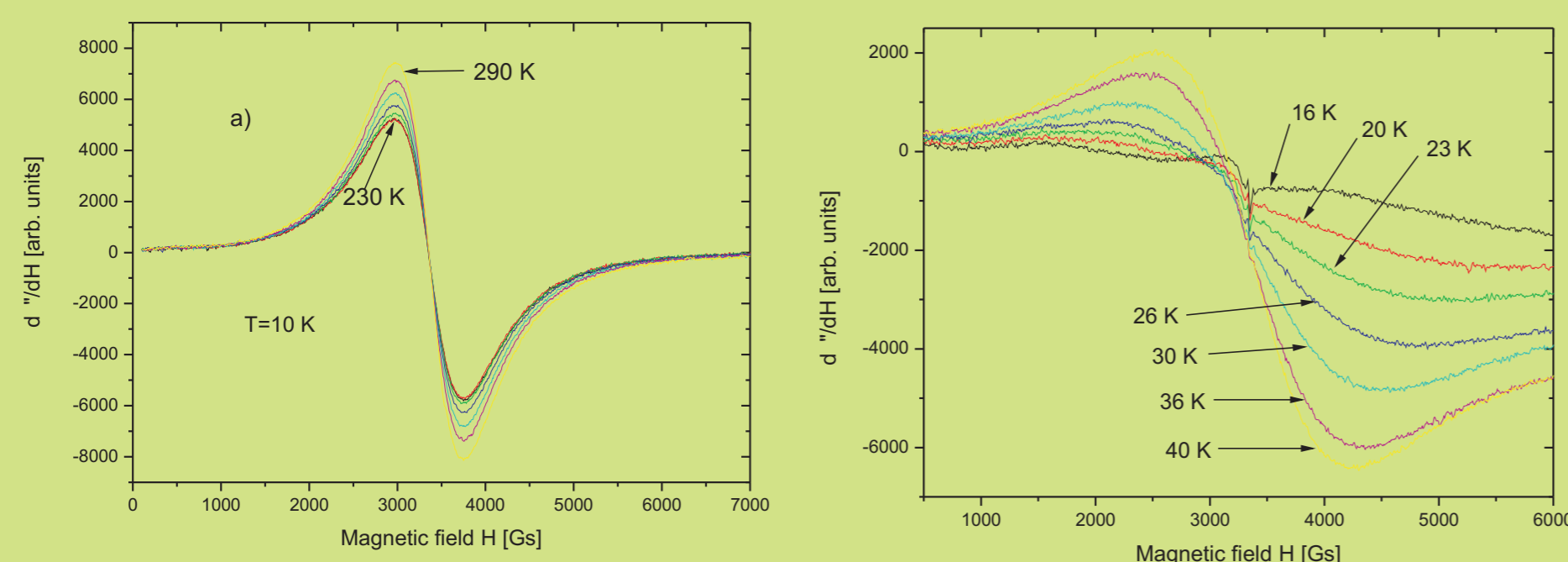


Figure 1. Temperature dependence of the EPR/FMR spectra of the $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ compound. Left panel-high temperature range, $T \geq 230$ K; right panel-low temperature range, $T \geq 40$ K.

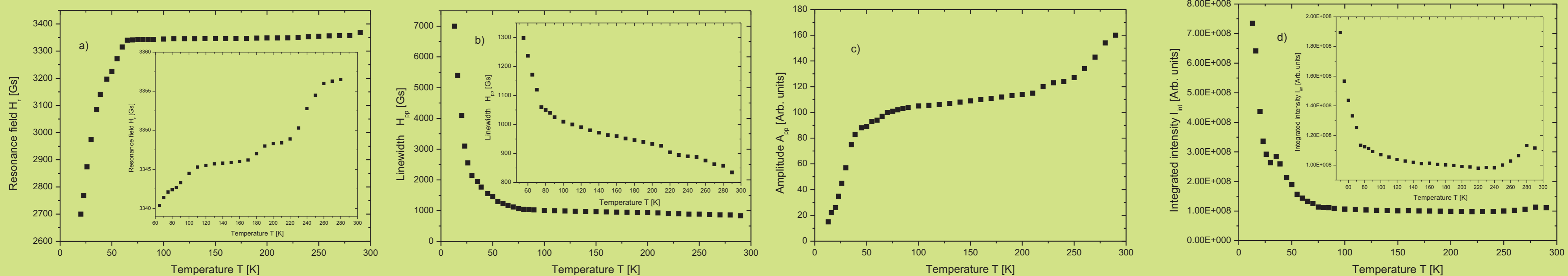


Figure 2. Temperature dependence of the resonance line parameters: resonance field $H_r(T)$ (a), linewidth $\Delta H_{\text{pp}}(T)$ (b), signal amplitude A_{pp} (c), integrated intensity I_{int} (d), and reciprocal of integrated intensity $1/I_{\text{int}}$ (e).

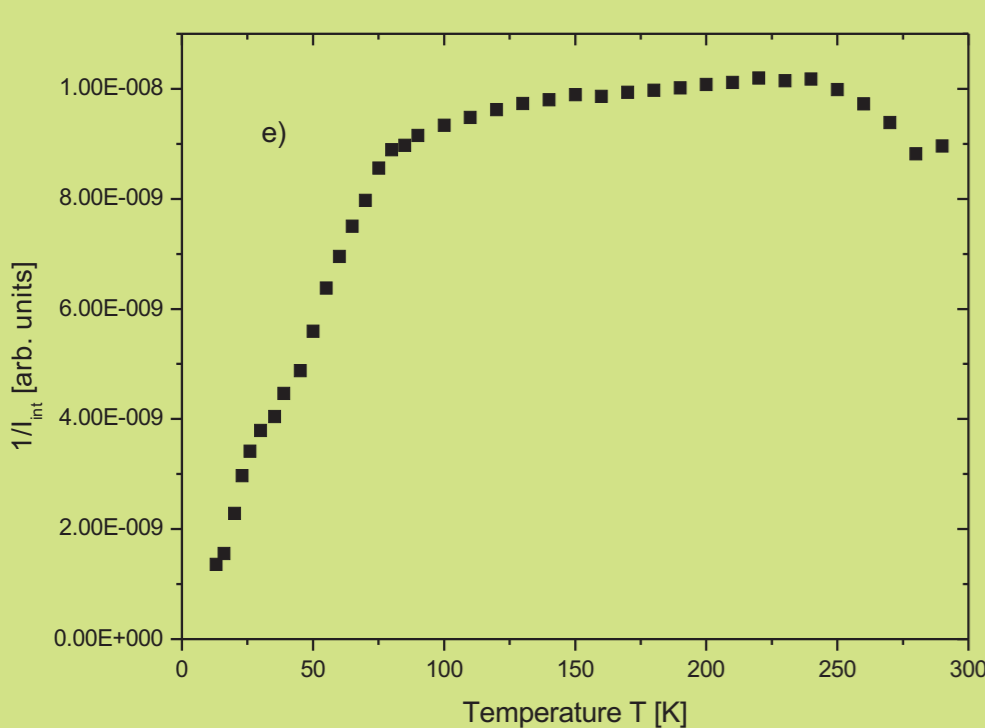


Table 1 The resonance field H_r , peak-to-peak linewidth ΔH_{pp} at room temperature and the temperature gradient of the resonance field $\Delta H_r/\Delta T$ for various compounds in M-Fe-V-O system.

Compound	H_r [Gs]	ΔH_{pp} [Gs]	$\Delta H_r/\Delta T(290-240 \text{ K})$ [Gs/K]	$\Delta H_r/\Delta T(40-20 \text{ K})$ [Gs/K]
$\text{Zn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [13]	3361(1)	1207(1)	0.11	30.0
$\text{Mg}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [9]	3375(1)	1571(1)	0.08	28.0
$\text{Mn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [12]	3375(1)	637(1)	0.11	20.0
$\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ [10]	3357(1)	1072(1)	0.17	
$\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$	3358(1)	835(1)	0.16	21.0

Conclusions

The EPR/EMR study of new polycrystalline multicomponent 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. Additional magnetic sublattice could be formed in this compound with magnetic momentum "strength" intermediate between that registered for manganese(II) and copper(II) vanadate compounds. The observed thermal dependence of spectral parameters for $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ indicates on a large size of magnetic clusters appearing in the studied compound.

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Results and discussion

Figure 1 presents the temperature dependence of EPR/FMR spectrum of $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ powder sample. An almost symmetrical resonance line is observed at high temperatures. The registered EPR line at room temperature is centred at $g_{\text{eff}}=2.0007(3)$ (resonance field $H_r=3358(1)$ Gs) with peak-to-peak linewidth $\Delta H_{\text{pp}}=835(1)$ Gs. As the temperature decreases the amplitude of the line decreases and the linewidth slowly increases. Below 50 K the line becomes asymmetrical and a strong shift of the resonance field H_r is observed (Fig. 2). The derivative spectra were fitted to a full Lorentzian line comprising also the tail of the resonance absorption at negative fields, a consequence of the linearly polarized microwave field that becomes important when the width becomes comparable to the resonance field, as in the present case. Down to 4 K the presence of isolated Fe^{3+} ions in the high spin d^5 state ($^6S_{5/2}$ ground state) has not been recorded. The resonance field is almost similar to that registered for the $\text{Zn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ compound. The value of the linewidth falls between those measured for samples containing two different magnetic ions in the crystal lattice. The same trend for the temperature gradient of the resonance field at high temperatures is observed (Table 1). The replacement of cations by "stronger" magnetic ions could indicate a more effective exchange narrowing. The temperature gradient of resonance field in the high temperature range in $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ is comparable to that found in $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$. It could be suggested that inside the $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ structure an additional magnetic sublattice has appeared. Below 50 K the temperature gradient of resonance field increases over two orders of magnitude and is similar to that found for other compounds in $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ system with non-magnetic cations (Table 1).

The temperature dependence of the linewidth in $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ has shown marked differences in two temperature regions: at temperatures above ~ 70 K only a small increase of linewidth with temperature decrease is seen, while below that temperature a strong increase of linewidth is observed (Fig. 2b). The dipole-dipole magnetic interaction is supposed to be intense below ~ 70 K and at the same time the reorientation process is causing a strong change of the temperature gradient of the resonance field (Fig. 2a).

The amplitude of the resonance line decreases with temperature decrease and the thermal amplitude gradient, $\Delta A_{\text{pp}}/\Delta T$, has the following values in three temperature ranges (Fig. 2c): $\Delta A_{\text{pp}}/\Delta T(290-210 \text{ K}) \sim 0.6$ (1/K), $\Delta A_{\text{pp}}/\Delta T(210-85 \text{ K}) \sim 0.1$ (1/K) and $\Delta A_{\text{pp}}/\Delta T(50-13 \text{ K}) \sim 3$ (1/K). A very small value of $\Delta A_{\text{pp}}/\Delta T$ in the intermediate temperature range could be explained by assuming the presence of a "blocking" process, similar to what is observed in magnetic nanoparticles system. The spin clusters assumed to be present in $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ are playing the role of nanoparticles. Figure 2d presents the temperature dependence of the integrated intensity $I_{\text{int}}(T)$. The integrated intensity is calculated as the area under the absorption line and is proportional to the magnetic susceptibility of an investigated spin system. At high temperatures it slowly decreases with decreasing temperature but below 70 K an essential increase of $I_{\text{int}}(T)$ is registered. The thermal behaviour of integrated intensity and amplitude suggests that magnetic spin clusters of large sizes are formed in $\text{Cd}_4\text{Fe}_8\text{V}_{10}\text{O}_{41}$ [14].