

ANOMALOUS BEHAVIOR OF THE EPR SPECTRA OF $Zn_2CrV_3O_{11-x}$ COMPOUND

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Abstract: Two types of samples were investigated: annealed and non-annealed samples of $Zn_2CrV_3O_{11-x}$ compound. The annealed sample showed the presence of V^{4+} ions in the EPR spectra. Both types of samples gave evidence of $Cr^{2+} - Cr^{3+}$ pairs in magnetic resonance response.

I. INTRODUCTION

Multicomponent vanades and their polymorphic modification attract particular interest due to their catalytic properties and rich variety of structural and complex magnetic properties stemming from cation disorder in their crystal structure [1]. Magnetic frustration effects caused by mixed valence state of vanadium are also expected [2]. A new vanadate compound, $Zn_2CrV_3O_{11-x}$, is isostructural with $Zn_2FeV_3O_{11-x}$: its crystal structure is built from $M(1)O_6$ and $M(2)O_6$ octahedra, $M(3)O_5$ and $V(2)O_5$ trigonal bipyramids and two types of VO_4 tetrahedra [3]. The chromium atoms are disordered with zinc atoms on two or all three possible sites [M(1), M(2), and M(3)]. In this work we have attempted to study the magnetic interactions and spin dynamics in the metal ions sublattices.

II. RESULTS AND DISCUSSION

Polycrystalline $Zn_2CrV_3O_{11-x}$ samples have been synthesized by a solid-state reaction method. An X-ray analysis allowed to calculate the following lattice parameters: $a=0.6277(2)$, $b=0.7038(9)$, $c=1.1006(2)$, $\alpha=114.17(3)^\circ$, $\beta=101.27(5)^\circ$, $\gamma=101.89(6)^\circ$, $Z=2$ in the triclinic space group [4]. The electron paramagnetic resonance (EPR) spectra were recorded for both non-annealed and annealed samples, using a Bruker E 500 X-band spectrometer. During annealing the sample was held at a temperature of 750 K in two hours in oxidizing atmosphere. The temperature dependence of EPR spectra was performed in the temperature range of 4 to 300 K using an Oxford helium gas flow cryostat.

Fig. 1 shows representative EPR spectra detected at 4.6, 14 and 289 K. Two different EPR lines dominate the spectra: a wider and more intense line observed at high temperatures ($T > 8$ K) and a weaker and narrower Lorentzian-shaped line at low temperatures ($T < 8$ K). The low temperature resonance line centered at 345 mT can be most clearly discerned below 8 K. It could be attributed to V^{4+} ions ($3d^1$, $S=1/2$). In the whole temperature range its g values and linewidth remain nearly constant ($g_{\parallel}=1.941$, $g_{\perp}=1.973$, $\Delta B_{eff}=7.0$ mT). Its EPR integral intensity I , obtained by numerical integration of the absorption line, as a function of temperature strictly follows the Curie law (Fig. 2). The obtained linewidth, g_{\parallel} and g_{\perp} are in good agreement with results reported by Fuks et.al [5] investigating isostructural $Mg_2CrV_3O_{11-x}$ compound and other reports concerning vanadyl centres in different compounds [6,7,8,9]. It is true that the EPR spectrum of VO^{2+} ions usually contain seven

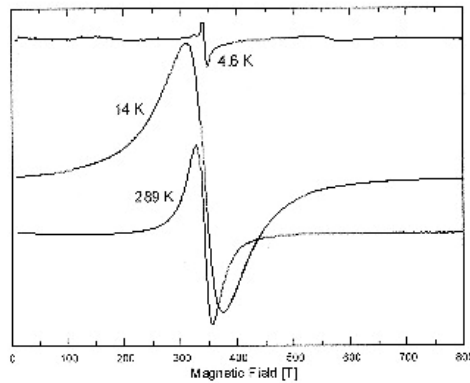


Fig 1. EPR spectra of $Zn_2CrV_3O_{11-x}$ at three selected temperatures.

narrow lines due to the hyperfine splitting (hfs) ($I=7/2$). In the investigation of non-annealed sample a hyperfine structure was not observed. After annealing the sample in oxygen this line splits in a characteristic way for V^{4+} ions. These results indicate on the direct relation between the number of V^{4+} ions and the splitting of the spectra. The lack of hfs seen in Fig. 1 is a result of strong superexchange of V^{4+} ions with V^{3+} ions through oxygen ions. The appearance of hfs is connected with weakening of the superexchange between V^{4+} and V^{3+} ions with lower number of V^{4+} ions due to the reaction $V^{4+} + \text{hole} \Rightarrow V^{3+}$. It's not curious and this was reported for many different compounds. The lack of hfs is connected with a high concentration of paramagnetic centres or with the delocalization of unpaired electrons [9]. In sufficiently high concentration of paramagnetic ions the dipolar and exchange interactions can overleap hyperfine structure and as a result only one EPR line is observed.

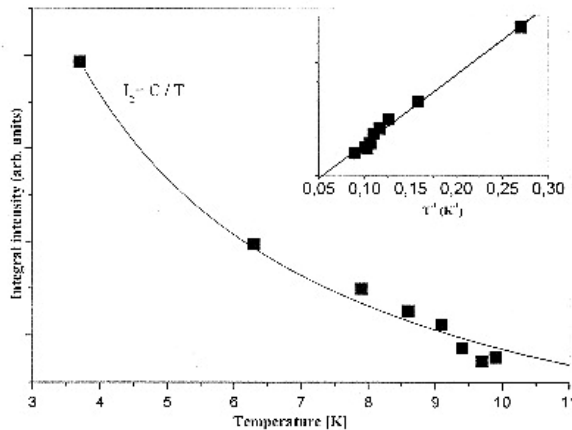


Fig 2. Integral intensity of a narrow line in $Zn_2CrV_3O_{11-x}$. Inset shows integral intensity vs. T^{-1} and a linear fitting of the experimental points.

The high temperature range is dominated by a broad and very intense line. As the temperature is lowered from 300 K, its intensity increases, reaching a maximum at $T=16$ K

and then decreases drastically towards zero (Fig. 3). The behavior of the intensity for annealed and non-annealed samples is similar within the limits of experimental error. Specific maximum of the line intensity and further disappearing in low temperatures can't be attributed to the isolated Cr^{3+} ions. The maximum in $I(T)$ indicates on the onset of a long range AFM ordering and can be interpreted as transitions within thermally populated excited state levels of the nearest-neighbor spin-coupled Cr^{3+} pairs (chromium dimers) [10]. As the temperature increases, the Cr^{3+} magnetic moments experience the short-range AFM correlations, evidenced by no temperature g -shift (Fig. 4) ($g=1.97441(166)$ and $g=1.97275(261)$ for annealed and non-annealed samples, respectively). Behavior of intensity in the high temperature range could be treated as typical for paramagnetic centers and described by the Curie-Weiss relation. The expected temperature dependence of the integral EPR intensity for dimers $S=3/2$, which is proportional to the magnetic susceptibility, is given by the Fournier formula [11,12]:

$$I(T) \sim \frac{C}{kT} \frac{\exp(x) + 5\exp(3x) + 14\exp(6x)}{1 + 3\exp(x) + 5\exp(3x) + 7\exp(6x)} \quad (1)$$

where $x=2J/kT$ and $C=2Ng^2\mu_B$. The solid line in Fig. 3 shows the temperature dependence given by the above equation with $2J/k=9.5(5)$ K. Similar interaction between Cr^{3+} ions have been observed in ZnCr_2O_4 compound [13] and identical dependence of EPR integral intensity vs. temperature was received.

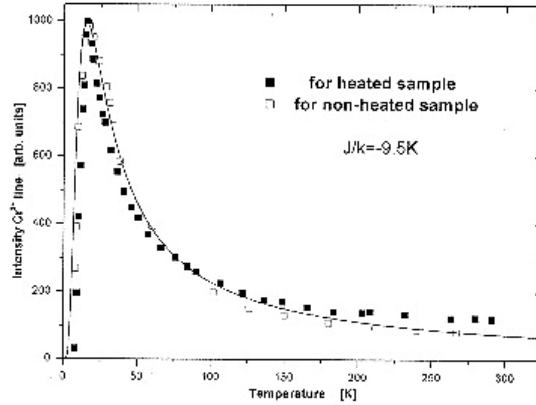


Fig 3. The temperature dependence of the integral EPR intensity for the high-temperature line.

Fig. 5 presents the temperature dependence of the effective EPR peak-to-peak linewidth ΔB_{eff} . Behavior of linewidth for both samples is nearly identical. As the temperature is lowered from 300 K, ΔB_{eff} displays a linear behavior. Then the linewidth goes through a minimum at $T=38$ K and increases drastically while approaching the transition temperature to the magnetically ordered state. The linear increase could be explained by interactions of spins with the charge carriers. This case is known as a bottleneck regime [14] and means that coupled pairs under EPR experiment are unfit to transfer microwave energy to the lattice. The hopping rate of charge carriers limits the lifetime of the spin state. This leads to broadening of the EPR line, proportional to the hopping rate. As temperature increases, the relaxation is proportionally faster and thus larger linewidth is observed. Experimental points of temperature dependence of the linewidth were simulated by a modified Huber equation [15]:

$$\Delta B = a \left(\frac{T - T_N}{T_N} \right)^b + cT + \Delta B_0$$

with the following values: $c=0.043(2)$ mT/K, $b=1.96(9)$, $T_N = 5.9(6)$ K and $\Delta B_0 = 15.8$ mT (solid line in Fig. 5).

According to chemical circumstances the vanadium ions in fully-oxidized $Zn_2CrV_3O_{11-x}$ compound could be in a diamagnetic V^{5+} state. The existence of V^{4+} ions suggests that indeed the mentioned sample is oxygen-deficient. Lack of oxygen in some crystallographic positions locally changes an electronic equilibrium, i.e. one oxygen electron is attracted to vanadium and V^{4+} (or VO^{2+}) paramagnetic state is created. Oxygen-deficiency creates the V^{4+} valence state, so the total electrochemical equilibrium is kept.

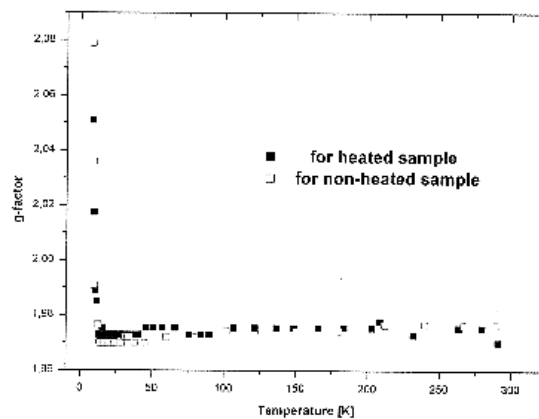


Fig 4. Temperature dependency of g-value of the high-temperature EPR

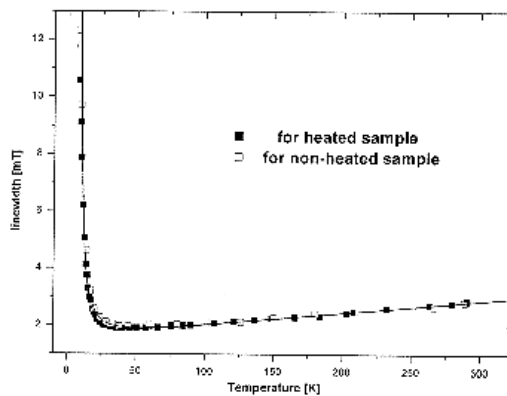


Fig 5. Temperature dependence of the EPR linewidth for the high-temperature line.

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