

# Magnetic study of $\text{Cr}^{3+}$ ion in $M_2\text{CrV}_3\text{O}_{11-x}$ ( $M=\text{Zn}, \text{Mg}$ ) compounds

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## Abstract

Electron paramagnetic resonance (EPR) and magnetic susceptibility measurements on the recently synthesized vanadates  $M_2\text{CrV}_3\text{O}_{11-x}$  ( $M = \text{Zn}, \text{Mg}$ ) have been analyzed. Two absorption lines with  $g \approx 2.0$  (type I) and  $g \approx 1.98$  (type II) were recorded in the EPR spectra, which can be attributed to  $\text{V}^{4+}$  ions and  $\text{Cr}^{3+}$  ion clusters (pairs), respectively. The exchange constant  $J$  between  $\text{Cr}^{3+}$  ions has been calculated, using both EPR and magnetic susceptibility data. Fitting of the EPR and magnetic susceptibility data has been carried out. The sign of  $J$  is a negative one for all samples and indicates antiferromagnetic interactions. Some difference in the  $J$  constant value among samples has been obtained. Volumetric titration confirms distinctly the presence of vanadium  $\text{V}^{4+}$  ions in the investigated compounds.

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**Keywords:** Chromium vanadates with Zn; Mg; Structure; EPR; Magnetic susceptibility; Chromium pairs

## 1. Introduction

Multicomponent vanadates and their polymorphic modification attract particular interest due to their catalytic properties enabling their greater comprehensive application in industrial practice as active and selective catalysts in many processes of oxidative dehydrogenation of lower alkanes [1]. Dehydrogenation is usually performed over catalysts containing vanadyl ions on various supports. It is generally accepted that the reaction proceeds by the abstraction of a hydrogen from the alkane and reduction of a tetrahedrally coordinated  $\text{V}^{5+}$  species [2]. The presence of isolated  $\text{VO}_4^{3-}$  anions in magnesium orthovanadate or corner-shared  $\text{VO}_4$  tetrahedra in the pyrovanadates could be satisfyingly investigated using the electron paramagnetic resonance spectroscopy (EPR) technique. Rich variety of structural and complex magnetic properties stemming

from cation disorder in their crystal structure [3,4] and magnetic frustration effects caused by mixed valence state of vanadium are also expected [5]. New ternary vanadates of  $M_2\text{CrV}_3\text{O}_{11-x}$  ( $M=\text{Zn}, \text{Mg}$ ) type being formed in the  $\text{MO}-\text{V}_2\text{O}_5-\text{Cr}_2\text{O}_3$  ( $M=\text{Zn}, \text{Mg}$ ) systems have recently been obtained [6,7]. These compounds crystallize in the triclinic system and only the basic crystallographic parameters have been determined up to now. The structures of  $\text{Zn}_2\text{FeV}_3\text{O}_{11-x}$  and  $\text{Mg}_2\text{FeV}_3\text{O}_{11-x}$  compounds, which belong to the multicomponent vanadate group, have been obtained from neutron diffraction [8,9] and X-ray diffraction [10]. Their crystal structure is built of  $M(1)\text{O}_6$  and  $M(2)\text{O}_6$  octahedra,  $M(3)\text{O}_5$  and  $V(2)\text{O}_5$  trigonal bipyramids, and two types of  $\text{VO}_4$  tetrahedra. The chromium atoms are disordered between two or all three possible sites [ $M(1)$ ,  $M(2)$ , and  $M(3)$ ]. Close equality of the values of the unit cell of the  $M_2\text{CrV}_3\text{O}_{11-x}$  ( $M=\text{Zn}, \text{Mg}$ ) compounds suggests that these compounds are isostructural. Their structural investigations are in progress.

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EPR investigations of  $3d$  ions have been extensively studied to obtain information on the degree of short-range ordering in disordered solids and identify the local site symmetry around  $3d$  ions. Among the above-mentioned investigations, one can find some EPR report of chromium ions, dispersed on different supports. Landry et al. [11] and Ardelean et al. [12,13] studied EPR spectrum and optical absorption of  $\text{Cr}^{3+}$  ions in glasses as a function of  $\text{Cr}_2\text{O}_3$  content. They evidenced that the EPR spectrum gradually changes with increase in the  $\text{Cr}_2\text{O}_3$  concentration, from an initial  $g \approx 4.0$  low-field absorption assigned to isolated, octahedrally coordinated  $\text{Cr}^{3+}$  ions, to another one at high field with a  $g \approx 2.0$ , attributed to exchange coupled pairs of  $\text{Cr}^{3+}$  ions, which are individually six-fold coordinated. The absence of low-magnetic-field EPR signal at high chromium concentration implies a very small splitting between the two Kramer states of  $\text{Cr}^{3+}$  ions existing at zero magnetic field. A similar conclusion has been obtained by Stadnyk et al. [14,15] who investigated  $\text{ZrNi}_{1-x}\text{Cr}_x\text{Sn}$  solid solution. They have detected two types of  $\text{Cr}^{3+}$  ion EPR resonances with  $g \approx 1.988$  and 2.06 that are also strongly dependent on temperature and chromium concentration. Ardelean et al. [13] also observed  $\text{Cr}^{5+}$  absorption line in EPR spectra with  $g \approx 1.97$ . They found that with increase in chromium oxide concentration a broad absorption due to the above-mentioned  $\text{Cr}^{3+}$  ion pairs overlaps the  $\text{Cr}^{5+}$  absorption single line. The  $g \approx 1.98$  absorptions caused by  $\text{Cr}^{5+}$  ions in octahedral symmetry were also detected in other glasses containing chromium ions [16,17]. Fournier et al. [18] elucidated the antiferromagnetic nature of  $\text{Cr}^{3+}$ -coupled pairs during their investigations of phosphate glasses. Precise studies of EPR spectra for nearest-neighbor  $\text{Cr}^{3+}$  pairs in different crystals have been performed by many authors [19–23]. They assigned EPR transitions in the spectrum to proper  $\text{Cr}^{3+}$  states with total spin  $\Sigma = 1, 2, 3$  and determined the parameters of these exchange interactions between  $\text{Cr}^{3+}$  ions.

In the present work, we attempted to study magnetic interactions and spin dynamics in metal ions sublattices of  $M_2\text{CrV}_3\text{O}_{11-x}$  ( $M=\text{Zn}, \text{Mg}$ ) compounds. Some results of the EPR spectroscopy of these materials were presented previously [24–26]. Also, magnetic susceptibilities were performed and compared for these two compounds.

## 2. Experimental

Polycrystalline powder samples of  $M_2\text{CrV}_3\text{O}_{11-x}$  ( $M=\text{Zn}, \text{Mg}$ ) compounds have been synthesized by a solid-state reaction method. Thorough descriptions of synthesis, crystallographic findings, melting temperatures and the way of melting, and also the infrared

absorption investigations have been collected in Refs. [6,7]. The EPR spectra were recorded for both non-annealed (in the air) and annealed samples using a Bruker E 500 X-band spectrometer. During the annealing, the samples were held at the temperature of 750 K for 2 h in oxidizing atmosphere. We registered the temperature dependence of EPR spectra in the temperature range of 4–300 K using an Oxford helium gas flow cryostat. Magnetic measurements were carried out using an MPMS-5 SQUID magnetometer. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements were performed in the temperature range of 2–300 K at constant magnetic field. The isothermal magnetization was measured versus temperature and magnetic field up to 50 kOe.

## 3. Results and discussion

### 3.1. Electron paramagnetic resonance measurements

Fig. 1 shows the temperature evolution of EPR spectra for  $\text{Zn}_2\text{CrV}_3\text{O}_{11-x}$  compound. Similar spectra have been detected for  $\text{Mg}_2\text{CrV}_3\text{O}_{11-x}$  compound. In both samples two different EPR lines dominate in the absorption spectra (Fig. 1): a wide and an intense one ( $g \approx 1.98$ ) and a weaker and narrower one ( $g \approx 2.0$ ), indicated as I and II types, respectively. As the temperature increases, II type line is not observed because it is strongly overlapped by the broad and very intense Lorentzian shape of I type line.

Temperature analysis of the linewidth of II type line and its  $g$ -factor  $g \approx 2.0$ , as we reported in an earlier work [24,25], allows us to attribute this line to  $\text{V}^{4+}$  ions or  $\text{VO}^{2+}$  centers. It stays in good agreement with the results of some papers concerning vanadium centers in other compounds [27–30]. One cannot associate this line

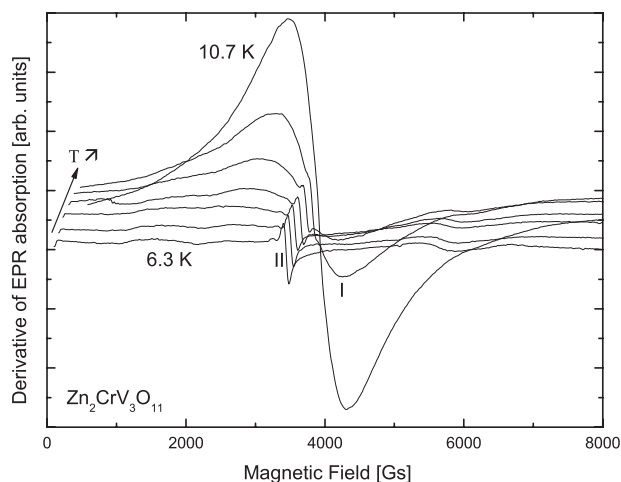


Fig. 1. Temperature evolution of EPR spectra for  $\text{Zn}_2\text{CrV}_3\text{O}_{11-x}$  compound.

to  $\text{Cr}^{5+}$  ions. Guskos et al. [4] registered the same type line in  $\text{Zn}_2\text{FeV}_3\text{O}_{11-x}$  compound and related it to paramagnetic defects. It is known that the EPR spectrum of  $\text{VO}^{2+}$  ions usually contains seven narrow lines due to hyperfine splitting (hfs) ( $I = 7/2$ ). Our non-annealed sample does not reveal a hyperfine structure. However, based on earlier investigations [24], after the annealing in oxygen, this line splits in a characteristic way as is usually observed for  $\text{V}^{4+}$  ions [31,32]. The lack of the hfs is a result of strong superexchange interaction of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions through the oxygen ions. The appearance of hfs is connected with the weakening of the superexchange interaction between  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions with the lower number of  $\text{V}^{4+}$  ions due to the following reaction:  $\text{V}^{4+} + \text{hole} \Rightarrow \text{V}^{5+}$ . Similar results have also been obtained for some other compounds [31,32]. Volumetric titration confirmed distinctly the presence of vanadium  $\text{V}^{4+}$  ions in the investigated compounds. Their solution was titrated with  $\text{KMnO}_4$  and the endpoint corresponded to the number of moles of  $\text{V}^{4+}$ :  $2.9344\text{E-}5$  moles per 1 mol of  $\text{V}^{5+}$  for  $\text{Mg}_2\text{CrV}_3\text{O}_{11}$  and  $4.4097\text{E-}5$  moles per 1 mol of  $\text{V}^{5+}$  for  $\text{Zn}_2\text{CrV}_3\text{O}_{11}$ . However, we cannot decide to use the results due to its low reproducibility (too high method error).

The I line with  $g \approx 1.98$  could be clearly observed for higher temperatures, i.e.,  $> 10$ ,  $> 15$  K, for  $(\text{Zn}, \text{Mg})_2\text{CrV}_3\text{O}_{11-x}$ . Fig. 2 shows the temperature behavior of integral intensity of the I line (symbols), estimated by double integration of the absorption. In all cases one can observe a weak, but well defined, maximum of the intensity at 15.4, 12.2 K for  $(\text{Zn}, \text{Mg})_2\text{CrV}_3\text{O}_{11-x}$ . Below these temperatures  $I(T)$  decreases continuously down to lower values suggesting that some antiferromagnetic correlations are present. It excludes responsibility of the

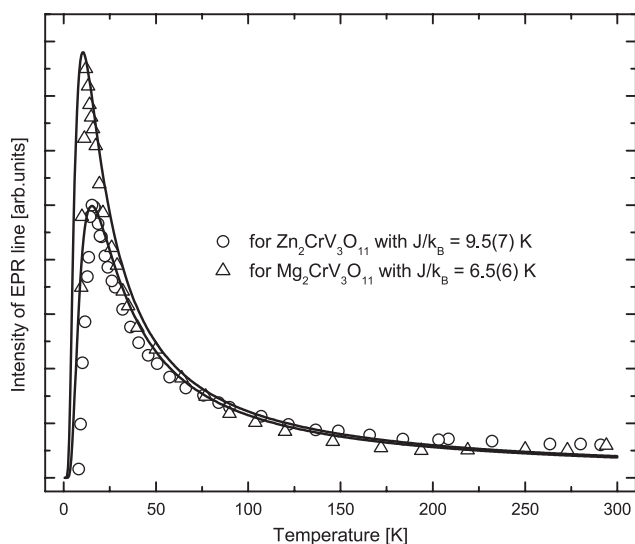


Fig. 2. Temperature dependency of the integral EPR intensity for  $\text{Cr}^{3+}$  line.

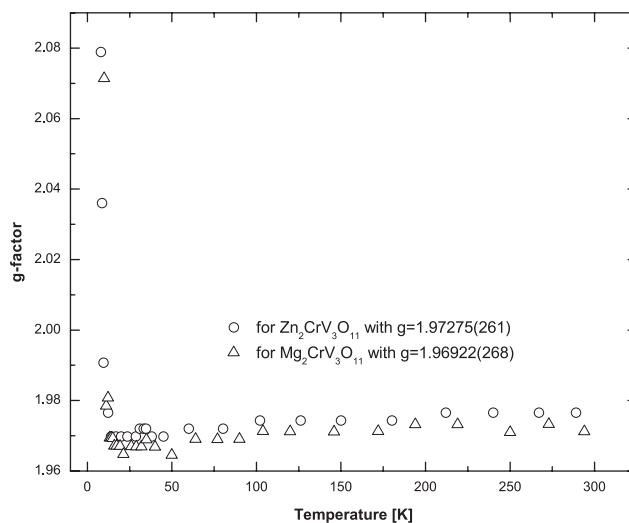


Fig. 3. Temperature dependency of  $g$  values for  $\text{Cr}^{3+}$  EPR line.

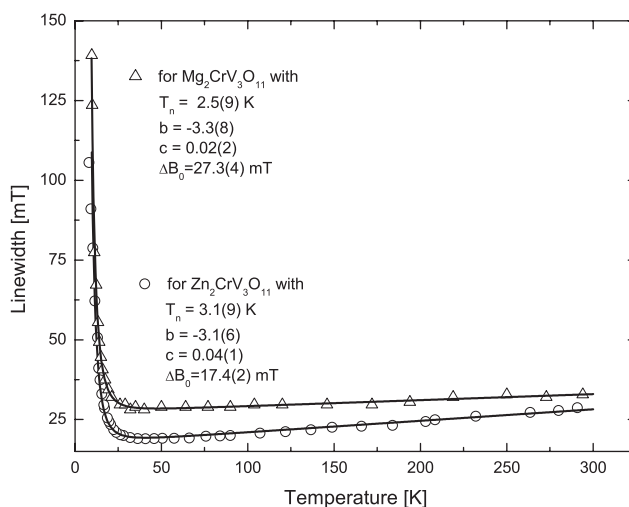


Fig. 4. Temperature dependency of the EPR linewidth for  $\text{Cr}^{3+}$  line.

single paramagnetic centers for these resonant lines (see also Static Susceptibility section of the paper). In the same temperature range the peak-to-peak linewidth,  $\Delta B_{\text{eff}}$ , (Fig. 3) increases substantially as the temperature is lowered, while in high temperatures one can observe an interesting linear progress of the  $\Delta B_{\text{eff}}$ . The average internal magnetic field at this temperature range is almost constant, evidenced by no temperature  $g$ -shift for all the samples (Fig. 4).

The presence of the wide and high intense EPR line with  $g \approx 1.98$  [11–15] could be attributed to  $\text{Cr}^{3+}$  clusters. Taking into account the intensity and peak-to-peak linewidth behavior versus temperature of the I type line, it could not to be attributed to the isolated  $\text{Cr}^{3+}$  ions. The specific maximum of the intensity line (see Fig. 2) and its further disappearance at low

temperatures indicate the onset of a long-range AFM ordering between magnetic centers with antiparallel spin ordering. Thus, we will try to interpret the obtained experimental results assuming I type line is associated with  $\text{Cr}^{3+}$  ion pairs.

Such a situation for the nearest-neighbor  $\text{Cr}^{3+}$  spin-coupled pairs [19] can take place, and the line with intense maximum could be attributed to transitions within thermally populated excited states (characterized by the total spin  $\Sigma = S1 + S2 = 0, 1, 2, 3$ ). Henning et al. [20] studied EPR spectra of the nearest-neighbor  $\text{Cr}^{3+}$  pairs in  $\text{ZnGa}_2\text{O}_4$  at two frequency bands in detail: X-band (9.9 GHz) and Q-band (32.5 GHz), and observed transitions within each of the spin multiplets  $\Sigma = 1, 2$ , and 3. They gave theoretical temperature dependence of the intensity of each transition and hence determined the parameters of exchange interactions. We applied these expressions and the accurate fitting of the experimental intensity data (see Eq. (1) and solid line in Fig. 2) shows that only transitions within the multiplets  $\Sigma = 2$  can be recognized. The  $\Sigma = 3$  lines are very difficult to find, since they are of an order less intense than  $\Sigma = 2$  transitions. It is not excluded, however, that in the EPR spectrum of our powder, some unidentified lines could be attributed to  $\Sigma = 3$  transitions. The  $\Sigma = 1$  transitions are not observable due to extremely small transition probabilities, and, moreover, large zero-field splitting ( $\approx 1 \text{ cm}^{-1}$ ) makes it necessary to record the transitions at  $\nu = 32.46 \text{ GHz}$  (Q-band EPR spectrometer) [20]. The expected temperature dependence of integral EPR intensity of the  $\Sigma = 2$  transitions for  $\text{Cr}^{3+}$  pairs is the following:

$$I(T)_{\Sigma=2} \approx \frac{C}{T} \frac{\exp(3x)}{1 + 3 \exp(x) + 5 \exp(3x) + 7 \exp(6x)}, \quad (1)$$

where  $x = J/k_B T$  and  $C = 2Ng^2\mu_B$ ,  $J$  is the exchange constant,  $k_B$  is the Boltzmann constant, and  $\mu_B$  is Bohr magneton. At high temperature, the term  $C/T$  is dominant, hence, one could say that  $I(T)$  obeys Curie law in high temperatures. The solid lines in Fig. 2 show the temperature dependence given by the above equation,  $I(T)$ , for  $(\text{Zn, Mg})_2\text{CrV}_3\text{O}_{11-x}$ . That is why we can determine the isotropic exchange constants,  $J$ , which are equal to  $J/k_B = -9.5(7)\text{K}$ ,  $-6.5(6)\text{K}$  for  $(\text{Zn, Mg})_2\text{CrV}_3\text{O}_{11-x}$ . Similar interactions between  $\text{Cr}^{3+}$  ions have been observed in  $\text{ZnCr}_2\text{O}_4$  compound [21]. In the EPR spectrum of nearest-neighbor  $\text{Cr}^{3+}$  pairs in  $\text{SrLaAlO}_4$  or  $\text{SrLaGaO}_4$  single crystals [22] only  $\Sigma = 2$  transitions and an identical dependence of the EPR integral intensity versus temperature were received.

An interesting behavior reveals the temperature dependency of the effective EPR peak-to-peak linewidth  $\Delta B_{\text{eff}}$  (Fig. 4). As the temperature is lowered from 300 K,  $\Delta B_{\text{eff}}$  shows a linear decrease, goes through a minimum and increases drastically while approaching the transition temperature to the magnetically ordered

state. We simulated experimental points of the temperature dependence of the linewidth by a modified Huber equation [33] (solid line):

$$\Delta B = a \left( \frac{T - T_N}{T_N} \right)^b + cT + \Delta B_0, \quad (2)$$

where the first term in (2) is dominant at low temperature and reflects the critical broadening of the resonance line with  $T_N$  being the Neel temperature and  $b$  the critical exponent, while the second dominates in high temperature, where  $c$  is the slope of  $\Delta B$ . The third term describes a residual linewidth that is temperature independent. The best-fitting parameters to experimental data are  $T_N = 3.1(9)\text{K}$ ,  $b = -3.1(6)$ ,  $c = 0.04(1)\text{mT/K}$ ,  $\Delta B_0 = 17.4(2)\text{mT}$  and  $T_N = 2.5(9)\text{K}$ ,  $b = -3.3(8)$ ,  $c = 0.02(2)\text{mT/K}$ ,  $\Delta B_0 = 27.3(4)\text{mT}$  for  $(\text{Zn, Mg})_2\text{CrV}_3\text{O}_{11-x}$ . At low temperature,  $T < 15\text{K}$ , where the exchange coupling interactions between  $\text{Cr}^{3+}$  ions became stronger, spin-spin relaxation time decreases with decrease in temperature, and hence the sudden increase in the linewidth is observed. A linear decrease in the peak-to-peak linewidth at high temperatures indicates possible interactions of the spins with the charge carriers [34], when the relaxations process of the localized spin to the lattice occurs via the conduction electrons. As the temperatures increase, the spin-lattice relaxation time is proportionally shorter and thus a larger value of  $\Delta B_{\text{eff}}$  is observed.

### 3.2. Static magnetization studies

Figs 5 and 6 show the temperature dependence of inverse magnetic susceptibility  $\chi^{-1}$  and in detail the field dependence at  $T < 60\text{K}$  (in the inset) for all the

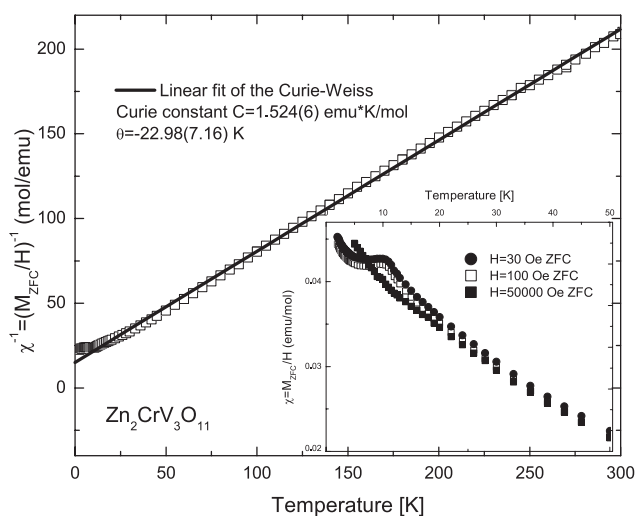


Fig. 5. Inverse magnetic susceptibility  $\chi^{-1}$  versus temperature for  $\text{Zn}_2\text{CrV}_3\text{O}_{11-x}$  compound. Solid line shows the best fitting by the Curie-Weiss law at high temperatures ( $T > 50\text{K}$ ). Inset shows behavior of the low-temperature ZFC magnetic susceptibility at magnetic fields up to 50 kOe.



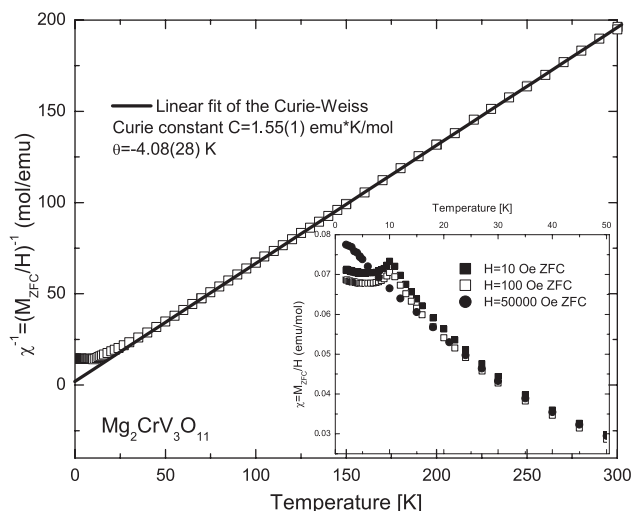


Fig. 6. Inverse magnetic susceptibility  $\chi^{-1}$  versus temperature for  $Mg_2CrV_3O_{11-x}$  compounds. Solid line shows the best fitting by the Curie–Weiss law at high temperatures ( $T > 50$  K). Inset shows behavior of the low-temperature ZFC magnetic susceptibility at magnetic fields up to 50 kOe.

investigated samples. The value of  $\chi^{-1}$  was derived from static magnetization measurements in the ZFC mode as  $M_{ZFC}/H$ . There was no difference between the susceptibility measured under FC and ZFC conditions. The magnetic susceptibility exhibits a weak maximum within low fields with significant field dependence at  $T_N = 11$  and 10 K for  $(Zn, Mg)_2CrV_3O_{11-x}$ . Below these temperatures it increases slightly as  $T \rightarrow 0$ . Typical antiferromagnetic behavior is the decrease in magnetic susceptibility towards zero as temperature approaches 0 K. In the high-temperature regime the behavior of  $\chi^{-1}$  is almost linear.

Here we attempt to give a quantitative analysis of the magnetic susceptibility measurements. As is shown in Figs 5 and 6, no apparent Curie term is observed in the low-temperature region, which means the presence of substantially magnetic  $V^{4+}$  or other paramagnetic impurity. EPR measurements have confirmed the presence of additional paramagnetic centers. For  $T > 50$  K the data can be fitted to the usual Curie–Weiss law. Parameters obtained from linear fit (solid line in Figs 5 and 6) are  $C = 1.524(6)$  emu K/mol,  $\theta = -22.98(7.16)$  K and  $C = 1.55(1)$  emu K/mol,  $\theta = -4.08(28)$  K for  $(Zn, Mg)_2CrV_3O_{11-x}$ . The effective magnetic moment of one mole of  $Cr^{3+}$  pairs calculated from Curie constant  $C$  is  $\mu_{\text{eff}} = 4.938(9)$  and  $4.979(2)$   $\mu_B$  for  $(Zn, Mg)_2CrV_3O_{11}$ . Expected values of  $\mu_{\text{eff}}$  for  $Cr^{3+}$  ion pairs are  $\mu_{\text{eff}} = 4.832(6)$  and  $4.823(7)$   $\mu_B$  for  $(Zn, Mg)_2CrV_3O_{11-x}$  where we used  $S = 2$  and  $g$  values (see Fig. 3) from EPR measurements. As is seen, the differences between both values of magnetic moments are only of the order of  $0.1 \mu_B$  and it seems that antiferromagnetically ordered spins could all be the

chromium spins. We suggest that the main contribution to total magnetic susceptibility arises from  $Cr^{3+}$  ion pairs with total spin  $S = 2$ . At low temperature, as the interactions between chromium pairs become AFM and non-Curie susceptibility goes to zero,  $V^{4+}$  or other paramagnetic centers contribute to total magnetic susceptibility. Hence, a slight increase in  $\chi^{-1}$  as  $T \rightarrow 0$  is predicted. The existence of  $V^{4+}$  ions suggests that indeed the mentioned sample is strongly oxygen deficient. According to chemical circumstances, the vanadium ions in the fully oxidized investigated compound could be in a diamagnetic  $V^{5+}$  state.

#### 4. Conclusions

EPR and magnetic susceptibility on the recently synthesized vanadates  $M_2CrV_3O_{11-x}$  ( $M = Zn, Mg$ ) provide experimental evidence that  $Cr^{3+}$  ions in the compounds form clusters, maybe pairs. The exchange constant,  $J$ , calculated by EPR measurements was  $J/k_B = -9.5$  and  $-6.5$  K for  $(Zn, Mg)_2CrV_3O_{11-x}$ . The sign of  $J$  is negative and indicates antiferromagnetic interactions. Different lattice constants of Cr–Cr distance lengths between the compounds can cause different values of the  $J$  constant. Accurate values of Neel's temperatures obtained from EPR data are  $T_N = 3.1(9)$  and  $2.5(9)$  K for  $(Zn, Mg)_2CrV_3O_{11}$ . Temperature dependence of the magnetic susceptibility also shows antiferromagnetic phase transition at  $T_N = 10$  and 11 K for  $(Zn, Mg)_2CrV_3O_{11}$ . The lack of decay of  $\chi(T)$  is caused by the presence of  $V^{4+}$  ions or other additional paramagnetic defects. The presence of vanadium  $V^{4+}$  ions in the investigated compounds has also been confirmed by volumetric titration. The existence of  $V^{4+}$  ions suggests that indeed strong oxygen deficiency can be present in  $M_2CrV_3O_{11-x}$  ( $M = Zn, Mg$ ) compounds.

Considering the absorption of the microwave energy in EPR measurements as being attributed to  $V^{4+}$  centers and  $Cr^{3+}$  pairs, an attempt of adjustment has been carried out (not included here). In the fitting procedure we took into consideration magnetic susceptibility arising from  $Cr^{3+}$  dimers [35]. Results of the fitting parameter exchange constant  $J$  agree enough with EPR measurements. At a high-temperature range, results of fitting agree very well with the experimental data for all the samples and could be effectively reduced to the Curie law. This also stays in agreement with the EPR measurements, in which only one EPR line is clearly observed at high temperatures. However, at low temperatures, below the temperature at which the interactions between  $Cr^{3+}$  pairs become AFM, the effect of the fitting procedure is not satisfactory. Based on the above, we draw a conclusion that chromium pairs do not form chromium dimers and that some clustered

system could be expected. To explain the behavior of magnetic susceptibility in the range of low temperatures we are going to use a cluster model.

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