

STRUCTURAL AND MAGNETIC CHARACTERIZATION OF THE Cr³⁺ AND Ni²⁺ ION SPECIES IN Ni₂CrV₃O₁₁

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Received: December 12, 2006

Abstract. Raman spectroscopic measurements have been carried out and compared for three ternary vanadate compounds: Mg₂CrV₃O_{11-x}, Zn₂CrV₃O_{11-x}, and Ni₂CrV₃O_{11-x}. Each compound gave a distinctive Raman spectrum dominated by the vanadium–oxo and chromium–oxo stretching bands in the 800–1000 cm⁻¹ region. Photoluminescence spectra have revealed possible cooperative emission bands of Ni²⁺ and Cr³⁺ ion pairs. Electron paramagnetic resonance (EPR) and magnetic susceptibility measurements of the Ni₂CrV₃O_{11-x} compound have been carried out and analyzed. The EPR spectra of the Cr³⁺-Ni²⁺ and Ni²⁺-Ni²⁺ pairs have been observed and confirmed by static molar magnetic susceptibility measurements. In order to describe the EPR spectra of interacting pairs, the spin Hamiltonian has been used in its usual form $-2J_{AB}S_A S_B$, but assuming a strong exchange limit. The temperature dependence of the magnetic susceptibility of Ni²⁺-Cr³⁺-Ni²⁺ trimers has been analyzed using standard Van Vleck formula. This analysis yielded an exchange constant, J_1/k_B , between Ni²⁺-Cr³⁺ of $-32(5)$ K, in good agreement with $J_{Cr-Ni}/k_B = -32(2)$ K calculated from the EPR results. Considerably positive exchange constant for Ni²⁺-Ni²⁺ species has been found, $J_2/k_B = 90(7)$ K. Assuming that local g -factors are isotropic, we have calculated local Zeeman factors $g_{Cr} = 1.977$ and $g_{Ni} = 2.157$, which are in good agreement with the values observed in the other Cr³⁺-Ni²⁺ complexes.

1. INTRODUCTION

The previous paper [1] reported magneto-spectroscopic studies on some members of a ternary vanadate series M₂CrV₃O_{11-x} (M = Zn²⁺, Mg²⁺), and provided evidence for the presence of significant antiferromagnetic interactions between Cr³⁺ ions. In particular, the electron paramagnetic resonance (EPR) spectrum of the nearest-neighbour Cr³⁺ spin-coupled pairs was measured with negative exchange constant J , as well that of the residual V⁴⁺

due to oxygen deficiency. The static magnetic susceptibility exhibited a weak maximum within low fields at low temperatures. Antiferromagnetic ordering was therefore indicated.

A new ternary vanadate of the M₂CrV₃O_{11-x} (M = Ni²⁺) type being formed in the NiO – V₂O₅ – Cr₂O₃ systems has recently been obtained [2,3]. This compound crystallizes in the triclinic system and only the basic crystallographic parameters have been determined up to now. Its crystal structure (taking isostructural vanadates M₂FeV₃O_{11-x}, M =

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Zn²⁺, Mg²⁺ [4,5]) consists of M(1)O₆ and M(2)O₆ octahedra, M(3)O₅ and V(2)O₅ trigonal bipyramids and two types of VO₄ tetrahedra. The chromium atoms are disordered between two or all three possible sites [M(1), M(2), and M(3)]. Each M3(O)5 bipyramid shares an edge with one M(2)O6 octahedron and a corner with one M(1)O6 octahedral dimer [6]. Based on crystallo-chemical consideration, it is common knowledge that the Cr³⁺ ion has the highest octahedral site preference of all the 3d metals (69 kJ/mol) [7]. In the event of full occupation of Ni²⁺ at trigonal (3) sites, the residual Ni²⁺ ions are forced to share the octahedral (1) and (2) positions with Cr³⁺, as the Ni²⁺ ions, just next to the Cr³⁺ ions, have the strongest preference for the octahedral sites (37.7 kJ/mol) [7]. Out of consideration for the cation distribution converged with mixed occupancies of Cr³⁺ and Ni²⁺ at the octahedral sites, one could conclude essential impact to exchange interactions between Ni²⁺ and Cr³⁺ ions.

This paper reports the results of EPR and static magnetic susceptibility study of Ni²⁺-Cr³⁺-Ni²⁺ trimers in the next member of the M₂CrV₃O_{11-x} series, namely M = Ni²⁺. It is clear that the M = Zn²⁺ and Mg²⁺ cations do not play a direct role in the exchange interactions [1]; however, they apparently modify the distances and angles between the molecular units, favoring modifications of the magnitude of exchange constant, *J*. In case of magnetic M = Ni²⁺ ion, one can expect some new exchange pathways and additional interactions affecting the magnetic properties.

2. EXPERIMENTAL

Polycrystalline powder samples of the Ni₂CrV₃O_{11-x} compound have been synthesized by a solid-state reaction method. Thorough descriptions of synthesis, crystallographic findings, melting temperatures, and the way of melting have been collected in [2].

All Raman spectra were collected under the control of Spex DM3000 microcomputer system using a conventional scanning Raman instrument equipped with a Spex 1403 double monochromator (with a pair of 1800 grooves/mm gratings) and a Hamamatsu 928 photomultiplier detector. The spectra were obtained in solid state at room temperature using the front-scattering geometry (135° angle) with 514.5 nm excitation, 100 mW laser power, and 6 cm⁻¹ slit widths. All samples were spun to avoid thermal decomposition. Sample pellets were prepared by mixing the compounds with dried anhydrous KCl.

Photoluminescence (PL) spectra for all the samples were measured at room temperature using a Specord-40 type spectrofluorimeter.

The electron paramagnetic resonance (EPR) spectra were recorded using a Bruker E-500 X-band spectrometer. The temperature dependence of EPR spectra was registered in the temperature range of 4 to 210K using an Oxford helium gas flow cryostat.

Magnetic measurements were carried out using a MPMS-5 SQUID magnetometer. Zero-field-cooled (ZFC) magnetization measurements were performed in the temperature range 2-300K at constant 100 Oe magnetic field.

3. RESULTS

3.1. Raman spectroscopic measurements

Fig. 1 displays the Raman spectrum of crystalline Ni₂CrV₃O_{11-x} in the 100–1100 cm⁻¹ region. In Figure 2 a comparison has been made between the Ni₂CrV₃O_{11-x} spectrum and those of the Mg₂CrV₃O_{11-x} and Zn₂CrV₃O_{11-x} compounds. The low frequency spectra in the region 100–700 cm⁻¹ are richly populated with weak Raman bands, most likely arising from metal–oxo deformation and crystal lattice vibrational modes. The largest difference among the three compounds occurs in the 550–650 cm⁻¹ region, where three Raman bands can be seen at 574, 609, and 624 cm⁻¹ for the Ni compound that are absent in the spectra of its Zn and Mg analogs. Thus, these bands can be attributed to the Ni centers of Ni₂CrV₃O_{11-x}.

The mid-frequency region above 700 cm⁻¹ contains metal–oxo stretching vibrations. The intense bands above 900 cm⁻¹ are assigned to stretching of the vanadium–oxo bonds, ν(VO). The ν(VO) stretch occurs as a single and sharp band at 922 cm⁻¹ in Ni₂CrV₃O_{11-x}, and is upshifted in Zn and Mg analogs to 943 and 959 cm⁻¹, respectively. The other intense Raman bands in this region occur for Ni₂CrV₃O₁₁ at 837, 856, and ~876 cm⁻¹. The sharp shoulder at 837 cm⁻¹ can be assigned to a nickel–oxo stretch, ν(NiO), whereas the other two bands at 856 cm⁻¹ and 876 cm⁻¹ may be due to the chromium–oxo stretching vibrations, ν(CrO).

3.2. Photoluminescence measurements

Fig. 3 shows room temperature photoluminescence (PL) spectra of the three vanadates. Three main

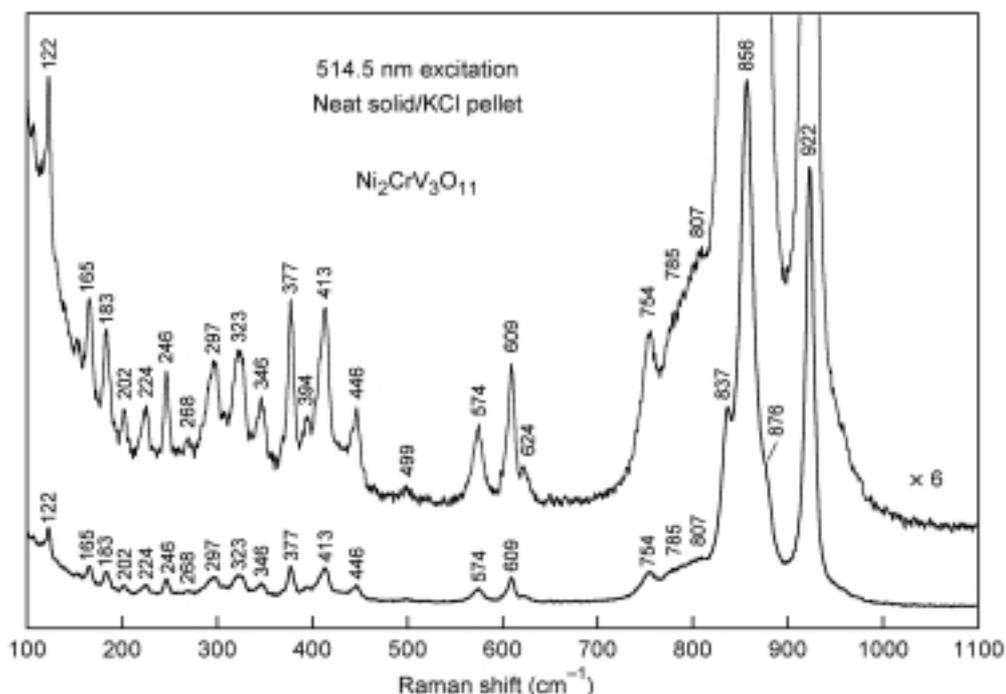


Fig. 1. Raman spectra of solid $\text{Ni}_2\text{CrV}_3\text{O}_{11-x}$ in the 100–1100 cm^{-1} region.

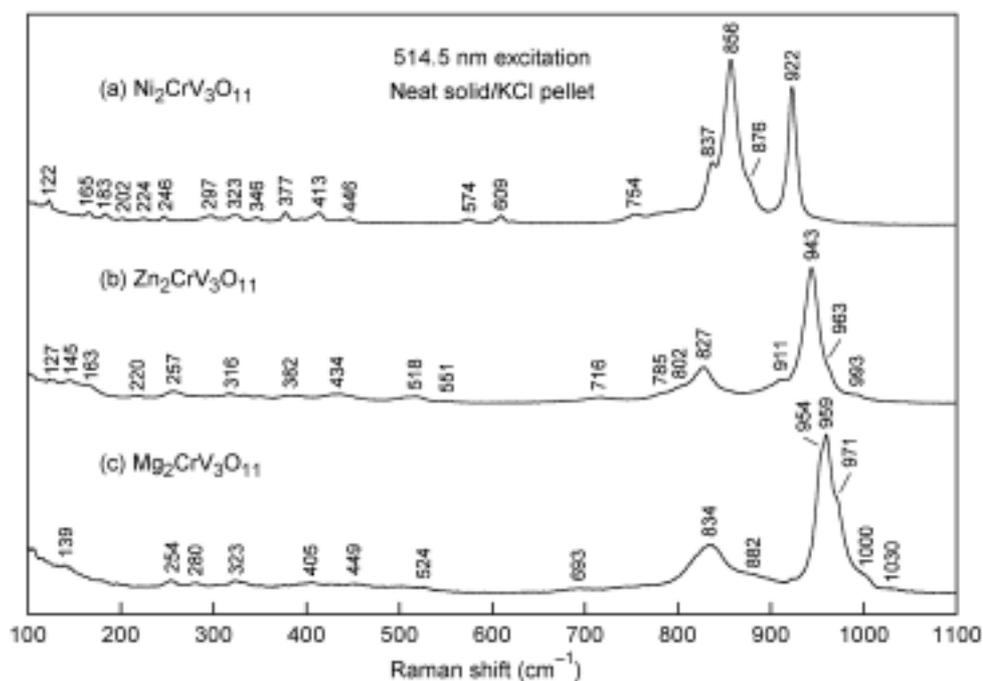


Fig. 2. Comparison of Raman spectra in the 100–1100 cm^{-1} region: (a) $\text{Ni}_2\text{CrV}_3\text{O}_{11-x}$, (b) $\text{Zn}_2\text{CrV}_3\text{O}_{11-x}$, and (c) $\text{Mg}_2\text{CrV}_3\text{O}_{11-x}$.

features of the spectra can easily be recognized in the range of 400–650 nm: two emissions centred at 468.1 and 601.1 nm for all three compounds and an additional emission peaking at 559.8 nm for the $\text{Ni}_2\text{CrV}_3\text{O}_{11-x}$ compound.

3.3. Electron paramagnetic resonance

X-band EPR spectra of polycrystalline $\text{Ni}_2\text{CrV}_3\text{O}_{11-x}$ were recorded over the temperature range 8–210 K to establish the electronic ground state for the Ni^{2+} -

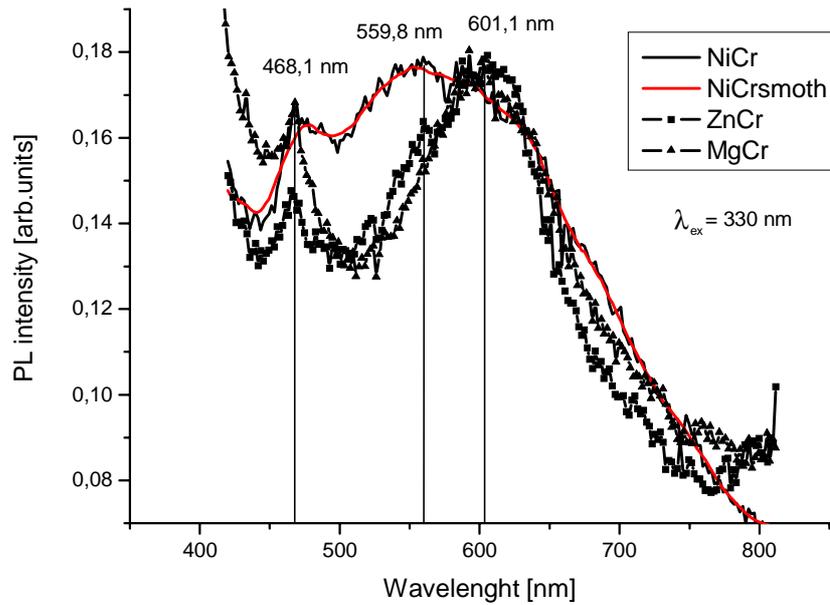


Fig. 3. Room temperature photoluminescence spectra of the indicated vanadate compounds.

Cr^{3+} species. Fig. 4 presents the first derivatives of the EPR signals at various temperatures (10–190K). As one can see there, three EPR lines could be recognized. The first, I-type, resonance line of the powder spectra is very broad and extends over a wide range from zero to more than 800 mT. An intensity of this signal decreases and an additional Lorentzian shape II-type line with $g = 1.857$ grows in with increasing temperature. Considerably weaker and narrower EPR III-type line with $g = 2.0$ can also be observed. As the temperature increases ($> 45\text{K}$), the III-type signal is overlapped by the constantly increased, intense II-type line. Similar III-type line have been detected in the previously investigated samples $(\text{Zn}, \text{Mg})_2\text{CrV}_3\text{O}_{11-x}$ [3]. Based on these observations, we associate the III-type line with the V^{4+} ions or VO^{2+} centers. The presence of low amount of the V^{4+} ions is due to some oxygen deficiency observed in the compounds and does not influence the magnetic interactions of Ni and Cr species.

The I- and II-type EPR lines require special attention and explanations, because their origin may be attributed to the presence of $\text{Ni}^{2+}\text{-Ni}^{2+}$ and $\text{Cr}^{3+}\text{-Ni}^{2+}$ pairs, respectively, and consequently, to the exchange pair interactions. In order to describe the EPR spectra of interacting pairs, the spin Hamiltonian has been used in its usual form, but assuming the exchange interaction, $-2J_{\text{AB}}\mathbf{S}_A \cdot \mathbf{S}_B$, to be

larger than all the other interactions, such as Zeeman, hyperfine one and zero field splitting (strong exchange limit – only in the case of II-type line) [see ref. 8].

It leads to low-lying states, the relative energies of which are given by the following equation: $E(\Sigma) = -J_{\text{AB}}[\Sigma(\Sigma+1) - S_A(S_A+1) - S_B(S_B+1)]$, where Σ denotes the spin of a given state and varies by an integer value from $|S_A - S_B|$ to $S_A + S_B$. S_A and S_B are the local spins of the interacting ions. J_{AB} is the exchange interaction parameter. The energy separation, $E(\Sigma) - E(\Sigma - 1)$, between adjacent levels, in considered limit, is assumed to be much larger than $h\nu$ of microwave radiation and no transition between states of different Σ will be observable. Therefore, the EPR spectrum of pairs is generally formed by one or more spectra arising from the spin multiplets Σ that are thermally populated at the temperature of experiment [9].

The I-type line is very difficult to analyze because it may arise from superposition of several lines originating from transitions inside and between different Σ states of $\text{Ni}^{2+}\text{-Ni}^{2+}$ dimers. Assumed by us model of strong exchange limit, due to weak $\text{Ni}^{2+}\text{-Ni}^{2+}$ interactions, cannot be useful in analyzing the I-type line. Hence, conclusions as to the origin of this line can be obtained only by taking into account the magnetochemistry results presented below.

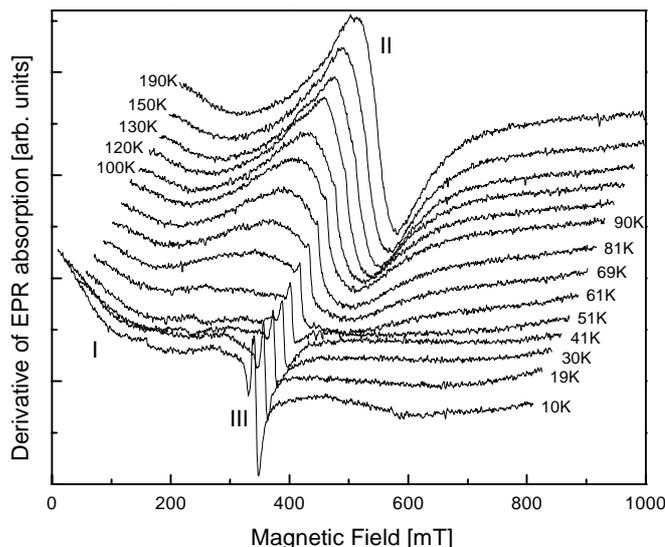


Fig. 4. The first derivatives of EPR signals for $\text{Ni}_2\text{CrV}_3\text{O}_{11-x}$ compound at various temperatures (10–190K).

Another situation takes place for the II-type line. The exchange interaction between the Cr^{3+} and Ni^{2+} ions forms a manifold of three levels of total spin $\Sigma = 1/2$ (at $5J_{\text{CrNi}}$), $3/2$ (at $2J_{\text{CrNi}}$) and $5/2$ (at $-3J_{\text{CrNi}}$), where the term in parentheses refers to the energies of a given level, in agreement with the above mentioned equation, $E(S)$. The temperature dependence of the integral intensity of II-type line (symbols in Fig. 5) is typical for the excited-state resonances of Cr^{3+} - Ni^{2+} pairs coming from a manifold

lying above the ground state, $\Sigma = 1/2$. Appreciable experimental errors of integrated intensities at low temperatures ($<70\text{K}$) are caused by the difficulty of selecting the II-type line from the entire spectrum. Nevertheless, one can observe in Fig. 5 a well defined maximum of the intensity at 70K. Below this temperature, $I(T)$ decreases continuously down to lower values suggesting that some anti-ferromagnetic correlations are present. Taking into account the above discussion, the accurate fitting

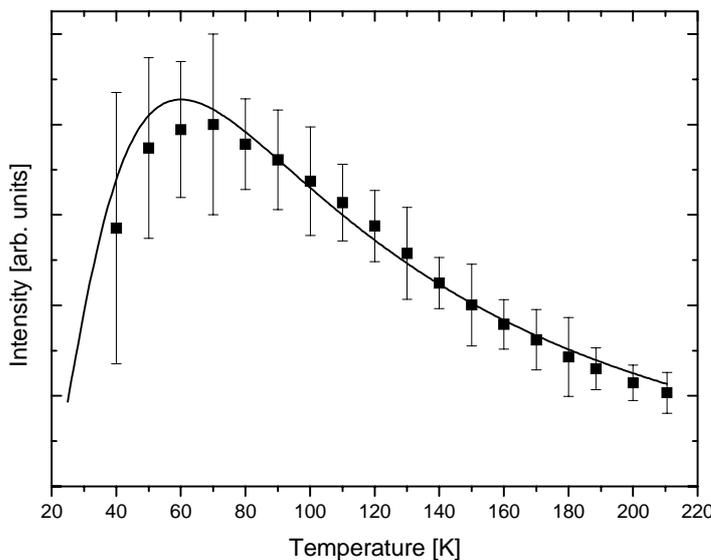


Fig. 5. Temperature dependence of the integral intensity for II-type EPR line (symbols) of $\text{Ni}_2\text{CrV}_3\text{O}_{11-x}$ and the fitting of the experimental data according to Eq. (1).

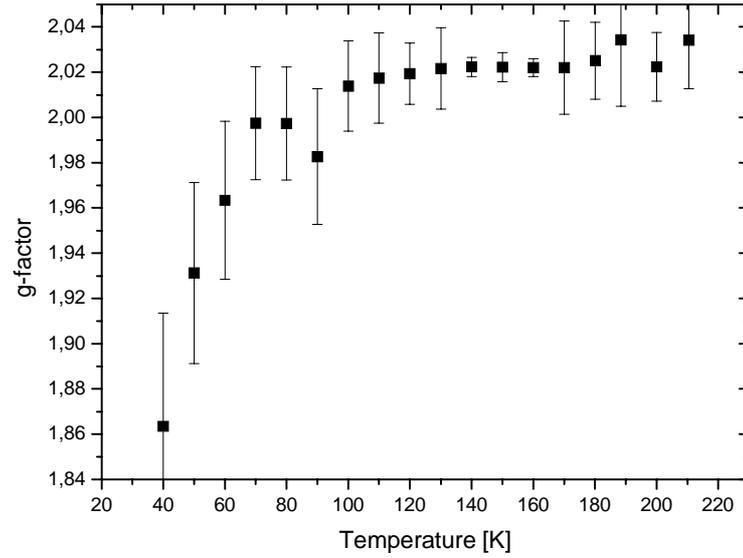


Fig. 6. The g -values for II-type line of Ni₂CrV₃O_{11-x} versus temperature.

of the experimental intensity data (solid line in Fig. 5) was performed for spin multiplets with $\Sigma = 3/2$ according to the following Boltzmann law [8]:

$$I \propto \frac{1}{T} \cdot \frac{\exp\left(\frac{3J_{CrNi}}{k_B T}\right)}{1 + 2 \exp\left(\frac{3J_{CrNi}}{k_B T}\right) + 3 \exp\left(\frac{8J_{CrNi}}{k_B T}\right)}. \quad (1)$$

From the above fitting we can find an isotropic exchange constant, J_{CrNi} , for interacting Cr³⁺ and Ni²⁺ ions, which equals $J_{CrNi}/k_B = -32(2)$ K.

No signal attributable to the $\Sigma = 5/2$ spin state was observed over the entire temperature range because of sufficiently large J_{CrNi} . It is not excluded, however, that the EPR spectrum of the II-type line at a given temperature can be also a superposition of the spectrum arising from the nondiamagnetic ground state, $\Sigma = 1/2$ and $\Sigma = 3/2$ state. As we previously stated, it is impossible to separate both lines in the spectrum. Actually, as one can see from Fig. 6, the g -values of the II-type line decrease from $g = 2.025$ at high temperature (210K) to $g = 1.857$ below 40K. At low temperatures all the Cr-Ni pairs should be in the ground state, therefore the Zeeman factor $g_{|1/2\rangle}$ for the $S = 1/2$ spin multiplet can be safely assumed to be equal to 1.857. Assuming that the local g -factors are isotropic and taking $g_{|3/2\rangle} = 2.025$ at high tem-

perature, we can calculate the local Zeeman factors g_{Cr} and g_{Ni} using the following relations [8,10]:

$$g_{|1/2\rangle} = \frac{5}{3}g_{Cr} - \frac{2}{3}g_{Ni}, \quad (2)$$

$$g_{|3/2\rangle} = \frac{11}{15}g_{Cr} + \frac{4}{15}g_{Ni}. \quad (3)$$

The obtained values of $g_{Cr} = 1.977$ and $g_{Ni} = 2.157$ are in good agreement with the values observed for the other Cr³⁺-Ni²⁺ complexes [11,12].

3.4. Magnetochemistry

Magnetic susceptibility data for polycrystalline samples of Ni₂CrV₃O_{11-x} were collected in the temperature range 2-300K. The data are displayed in Fig. 7 as molar magnetic susceptibility χ_T (right ordinate) and the magnetic moment μ_{eff} (left ordinate) versus temperature. At 300K, the μ_{eff} value is $5.50 \mu_B$ ($\chi_T = 3.78$ emu/mol K) and decreases monotonically with decreasing temperature until it reaches the value of $1.72 \mu_B$ ($\chi_T = 0.37$ emu/mol K) at 2K. This behaviour is typical of a system exhibiting dominant intramolecular antiferromagnetic exchange coupling [13]. At low temperatures the magnetic moment $\mu_{eff} = 1.7 \mu_B$ is appropriate for a system with a spin of 1/2 — ground state, i.e., the strong exchange interactions limit is valid. It seems to be due to coupled Cr³⁺-Ni²⁺ dimers with a nega-

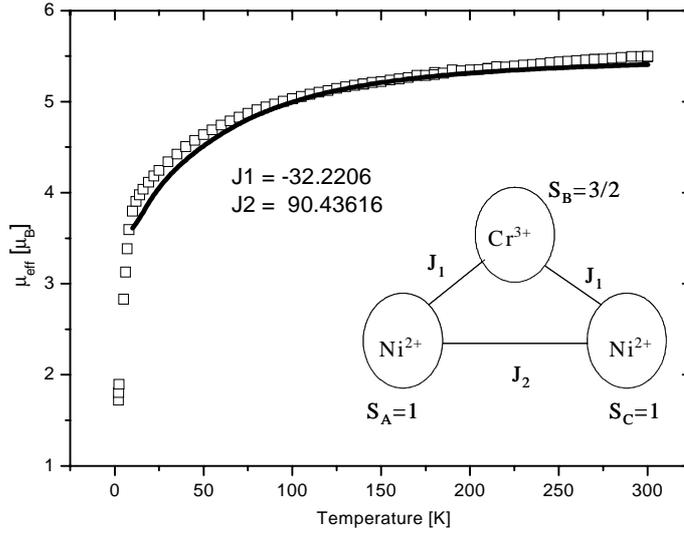


Fig. 7. The effective magnetic moment, μ_{eff} for polycrystalline samples of $\text{Ni}_2\text{CrV}_3\text{O}_{11-x}$ versus temperature.

tive exchange constant, J_{CrNi} . However, the μ_{eff} at high temperature is much larger than the value of $\mu_{eff} = 4.5 \mu_B$ expected for Cr^{3+} - Ni^{2+} species with average $g = 2.0$ [11]. We suggest that such a discrepancy can be explained by the additional exchange interactions coming from Ni^{2+} - Cr^{3+} - Ni^{2+} trimers, which lead to an increase of μ_{eff} in the entire 2–300K temperature range. Thus, the magnetic behaviour can be interpreted on the basis of an isotropic exchange Hamiltonian for trimers $S_A(\text{Ni}^{2+})$ - $S_B(\text{Cr}^{3+})$ - $S_C(\text{Ni}^{2+})$ (inset, Fig. 7).

The magnetic susceptibility of $\text{Ni}_2\text{CrV}_3\text{O}_{11-x}$ has been calculated using the standard formula for three linearly coupled spins that result from the isotropic spin-coupling Hamiltonian in an external magnetic field H along z direction:

$$\hat{H} = J_1(\hat{S}_A \cdot \hat{S}_B + \hat{S}_B \cdot \hat{S}_C) + J_2(\hat{S}_A \cdot \hat{S}_C) - g\mu_B \hat{H} \hat{S}_z \quad (4)$$

where J_1 is the exchange integral for Ni^{2+} - Cr^{3+} interactions and J_2 denotes the exchange interaction between Ni^{2+} - Ni^{2+} ions (see inset in Fig. 7). Magnetic susceptibility of metal ion Ni^{2+} and Cr^{3+} trimers has been found using standard Van Vleck formula [14], as a mean of the susceptibilities of the individual spin levels, each of them being weighted by its degeneracy. The corresponding results for the Ni^{2+} - Cr^{3+} - Ni^{2+} ($S_{\text{Ni}} = 1$ and $S_{\text{Cr}} = 3/2$) trimers can be expressed by:

$$\chi_m = \frac{N_A g^2 \mu_B}{3} \cdot \frac{F(J_1, J_2, T)}{k_B T} + \frac{A}{T}, \quad (5)$$

where:

$$F(J_1, J_2, T) = \frac{63 \exp\left(\frac{-3J_1 - J_2}{T}\right) + \frac{105}{4} \exp\left(\frac{-3/2J_1 + J_2}{T}\right) + \frac{15}{2} \exp\left(\frac{2J_2}{T}\right) + \frac{3}{4} \exp\left(\frac{9/2J_1 - J_2}{T}\right) + \frac{3}{4} \exp\left(\frac{5/2J_1 + J_2}{T}\right)}{4 \exp\left(\frac{-3J_1 - J_2}{T}\right) + 3 \exp\left(\frac{-3/2J_1 + J_2}{T}\right) + 2 \exp\left(\frac{2J_2}{T}\right) + \exp\left(\frac{-9/2J_1 - J_2}{T}\right) + \exp\left(\frac{5/2J_1 + J_2}{T}\right)} \quad (6)$$

and J_1 and J_2 are exchange constants for the Cr^{3+} - Ni^{2+} and Ni^{2+} - Ni^{2+} species, respectively. Other notations are those commonly used. The experimental values of χ_m have been fitted to the above equation by treating J_1 and J_2 as adjustable parameters. The resulting fitting of the effective magnetic moment μ_{eff} is shown as solid lines in Fig. 7, for which J parameters are $J_1/k = -32$ (5)K and $J_2/k = 90$ (7)K. As one can see, the value J_1 of exchange interaction between Ni^{2+} - Cr^{3+} ions agrees well with the EPR results.

4. DISCUSSION

In the Raman spectra we can observe distinct difference between the vibrational signature of Ni₂CrV₃O_{11-x} and those of Zn₂CrV₃O_{11-x} and Mg₂CrV₃O_{11-x}, which may result from different exchange interactions in all these compounds. In the latter two compounds, interactions among the Cr³⁺-Cr³⁺ pairs predominate [3], while in the former compound also Ni²⁺-Cr³⁺ and Ni²⁺-Ni²⁺ interactions may arise, forming the trimers S_A(Ni²⁺)-S_B(Cr³⁺)-S_C(Ni²⁺) (Fig. 7). The Ni₂CrV₃O_{11-x} exhibits other types of exchange interactions than the Zn and Mg trivanadates what is confirmed by the photoluminescence (PL) VIS spectra presented in Fig. 3 for $\lambda_{\text{ex}} = 330$ nm. Emitting centres in these compounds may involve impurity Cr centres, Ni impurity centres, tetrahedrally coordinated V-O moieties, and donor acceptor pairs, in addition to the possible presence of colour centres (including V_O, V_{Ni}, V_{Mg}, V_{Zn} vacancies). For Ni₂CrV₃O_{11-x}, a shoulder near 600 nm seems to be due to the chromium-related emission in slightly amorphous media [15], the 468.1-nm band seems to be a donor-acceptor pair emission [16], while the 559.8-nm band probably arises from the nickel-related emitting centre [17]. The bands at 468.1 and 601.1 nm may also be attributed to Cr and/or Ni cooperative emissions. Moreover, the 400-650 nm emission is characteristic of highly dispersed tetrahedrally coordinated V-O moieties in C_{3v} symmetry of highly dispersed catalysts due to charge-transfer processes involving an electron transfer from the O²⁻ to V⁵⁺ ions and a reverse radiative decay from the charge-transfer excited triplet state to its ground state [18].

In the EPR spectrum three lines dominate. Considerably weaker and narrower EPR III-type line with $g = 2.0$ is attributed to V⁴⁺ ions or VO²⁺ centers [3]. The I-type line we attributed to Ni²⁺-Ni²⁺ pairs as was expected from optical measurements. The fitting of the magnetic susceptibility shows that Ni²⁺ and Cr³⁺ are coupled with exchange constants $J_1/k = -32(5)\text{K}$ and $J_2/k = 90(7)\text{K}$. The magnitude of J_2/k confirms our conclusion that I-type line is a superposition of several lines originating from transitions involving different Σ states of the Ni²⁺-Ni²⁺ dimers, thereby, prohibiting us from applying a strong exchange limit approximation that allowed us to analyze the II-type EPR line.

Ni²⁺ and Cr³⁺ are antiferromagnetically coupled as well, but in this case we are dealing with a single EPR line for which we can use spin Hamiltonian in approximation of strong exchange limit. The Cr³⁺-Ni²⁺ pair has the $\Sigma = 1/2$ spin ground

state with the $\Sigma = 3/2$ level lying $\cong 73$ cm⁻¹ ($\cong 105\text{K}$) above it. The EPR spectra of the $\Sigma = 3/2$ level can be observed as II-type line over a wide range of temperatures (Fig. 4), and disappear slowly with decreasing temperature according to Eq. (1). Since the ground state is different from zero, it is highly probable that at low temperatures the $S = 1/2$ multiplet contributes to a total intensity of the II-type line. In consequence, below 40K, g -value changes to $g_{1/2>} = 1.857$. Assuming that the local g -factors are isotropic and taking $g_{3/2>} = 2.025$ at higher temperatures, we have calculated the local Zeeman factors $g_{\text{Cr}} = 1.977$ and $g_{\text{Ni}} = 2.157$. The accurate fitting of the magnetic susceptibility data (effective magnetic moment μ_{eff}) confirmed the presence of exchange interaction between Cr³⁺ and Ni²⁺ ions. Calculated exchange constant, $J_1/k = -32(5)\text{K}$, was found to be in good agreement with $J_{\text{CrNi}}/k = -32(2)\text{K}$ derived from the EPR data.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Professor Jolanta Kurzawa from the Department of Inorganic and Analytical Chemistry, Szczecin University of Technology, Poland for powder preparations and Professor Ritta Szymczak from the Institute of Physics Polish Academy of Sciences, Warsaw, Poland for susceptibility measurements. This work was partially supported by the grant No. 11-072-0120/17-88-00 (to S.M.K.) and by the Robert A. Welch Foundation (grant E-1184 to R.S.C.).

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