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## STUDY OF MAGNETIC DEFECTS IN $Nb_2VSbO_{10}$ AND $Nb_6VSB_3O_{25}$ COMPOUNDS

### Abstract

**Introduction and aim:** Two new compounds from the Nb-V-Sb-O system will be scrutinized as possible catalysts, because many compounds from this system has showed promising catalytic properties. Since there is often a direct link between the number of defects and catalytic activity of a compound, these two materials will be investigated by magnetic methods to detect existing defects and to determine their structure and properties.

**Material and methods:**  $Nb_2VSbO_{10}$  and  $Nb_6VSB_3O_{25}$  are relatively new compounds synthesized in Department of Inorganic and Analytical Chemistry, West Pomeranian University of Technology, Szczecin. Two magnetic methods have been used - dc magnetisation and electron paramagnetic resonance (EPR) spectroscopy.

**Results:** Although the nominal valences of metal ions in both compounds suggested non-magnetic properties, very complex magnetic response was registered in both magnetisation and EPR measurements. Non-homogeneous distribution of magnetic ions makes possible formation of different types of spin clusters and strongly interacting magnetic subsystems.

**Conclusion:**  $Nb_6VSB_3O_{25}$  seems to be more promising catalyst than  $Nb_2VSbO_{10}$  as there are more magnetic defects in this compound.

**Keywords:** Vanadium catalysts, magnetic properties, electron paramagnetic resonance.

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## BADANIE DEFECTÓW MAGNETYCZNYCH ZWIĄZKÓW $Nb_2VSbO_{10}$ i $Nb_6VSB_3O_{25}$

### Streszczenie

**Wstęp i cel:** Dwa nowe związki z układu Nb-V-Sb-O będą rozważane jako potencjalne katalizatory, gdyż wiele związków z tego układu wykazuje obiecujące właściwości katalityczne. Ponieważ często pomiędzy ilością defektów a aktywnością katalityczną istnieje zależność proporcjonalna, dwa te związki będą badane metodami magnetycznymi aby wykryć istniejące w nich defekty oraz określić ich strukturę i właściwości.

**Materiały i metody:**  $Nb_2VSbO_{10}$  and  $Nb_6VSB_3O_{25}$  zostały zsyntezowane stosunkowo niedawno w Katedrze Chemii Nieorganicznej i Analitycznej Zachodniopomorskiego Uniwersytetu Technologicznego w Szczecinie. Zastosowano dwie metody badania właściwości magnetycznych - stałoprądową magnetyzację i spektroskopii elektronowego rezonansu paramagnetycznego (EPR).

**Wyniki:** Chociaż nominalna wartościowość jonów metali w obu związkach sugeruje brak magnetycznych właściwości, zarejestrowano bardzo złożoną odpowiedź magnetyczną w pomiarach magnetyzacji i EPR. Niejednorodny rozkład jonów magnetycznych powoduje tworzenie się różnego rodzaju klastrów spinowych i silnie oddziaływujących podukładów magnetycznych.

**Wnioski:**  $Nb_6VSB_3O_{25}$  wydaje się być bardziej obiecującym katalizatorem niż  $Nb_2VSbO_{10}$ , ponieważ w tym związku jest dużo więcej defektów magnetycznych.

**Słowa kluczowe:** Katalizatory wanadowe, właściwości magnetyczne, elektronowy rezonans paramagnetyczny.

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## 1. Introduction

Catalysts based on vanadium oxide are used in several important industrial processes, e.g. oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in production of sulphuric acid, in oxidation of benzene to malefic acid, for selective reduction of  $\text{NO}_x$  with ammonia [7]. The use of additional metal oxides, beside vanadium oxide, improves the catalytic activity of the primary oxide. A large scientific literature is devoted to vanadium–antimony oxide catalysts that are applied in the processes of utilizing such air pollutants as hydrogen sulfide, carbon monoxide, or the oxides of nitrogen [2]. Thus it is expected that attractive catalytic properties would emerge in compounds formed from the oxides and phases containing niobium, vanadium, and antimony.

$\text{Nb}_2\text{VSbO}_{10}$  has been identified for the first time in the Nb-Sb-V-O system in year 2010 [3], while  $\text{Nb}_6\text{VSb}_3\text{O}_{25}$  was synthesized in the same laboratory in Department of Inorganic and Analytical Chemistry, West Pomeranian University of Technology, Szczecin, in year 2015 [4]. Both compounds crystallize in orthorhombic system, but detailed structure positions of constituting ions are not known due to difficulties of growing them in a single crystal form. If nominal valence of the four ions in both compound is assumed:  $\text{Nb}^{5+}$  ( $4d^0$ ),  $\text{V}^{5+}$  ( $3d^0$ ),  $\text{Sb}^{5+}$  ( $4d^{10}$ ),  $\text{O}^{2-}$  ( $2p^6$ ), they should display only weak diamagnetic properties. Magnetic properties of  $\text{Nb}_2\text{VSbO}_{10}$  and  $\text{Nb}_6\text{VSb}_3\text{O}_{25}$  were already investigated by using dc magnetization and electron paramagnetic resonance (EPR) techniques [5], [6]. dc magnetisation measurements in 2-290 K temperature range were done using an MPMS-7 SQUID magnetometer in magnetic fields up to 70 kOe in the zero-field-cooled (ZFC) and field-cooled (FC) modes. EPR spectroscopy was performed on a conventional X-band ( $\nu = 9.4$  GHz) Bruker E 500 spectrometer with the 100 kHz magnetic field modulations. The EPR measurements were carried in the 4-290 K temperature range using an Oxford Instrument helium-flow cryostat. The registered magnetic responses in magnetisation and EPR measurements were complex and indicated on substantial charge transfer from oxygen to metal ions in both compounds.

In this work the comparison of magnetic response of  $\text{Nb}_2\text{VSbO}_{10}$  and  $\text{Nb}_6\text{VSb}_3\text{O}_{25}$  will be compared and the similarities and differences will be discussed in terms of possibilities of these compounds to be used as useful catalysts. This compound that has more magnetic defects will be a more promising material in application as catalyst. The defects could appear as a result of charge transfer from oxygen to metal ions as well as existence of structural defects connected e.g. with grain boundaries.

## 2. DC magnetisation measurements

Temperature dependence of magnetic susceptibility  $\chi$  (defined as  $\chi = M/H$ ) of both compounds in an external magnetic field  $H = 10$  Oe is presented in figure 1. It is easy to notice that the value of susceptibility of  $\text{Nb}_2\text{VSbO}_{10}$  is roughly three order of magnitude weaker than of  $\text{Nb}_6\text{VSb}_3\text{O}_{25}$ . One of the reasons might be the higher number of metal ions in the later compound in the formulae unit (f.u.). It is also evident that  $\chi(T)$  could not be approximated by the Curie-Weiss law,  $\chi(T) = C/(T - T_{\text{CW}})$ , where  $C$  is the Curie constant and  $T_{\text{CW}}$  is the Curie-Weiss temperature. This indicates on the presence of a few magnetic subsystems in investigated samples. The sign of  $T_{\text{CW}}$  parameter provides information about kind of interaction between magnetic ions – negative sign signify antiferromagnetic interaction, positive sign ferromagnetic effective interaction.

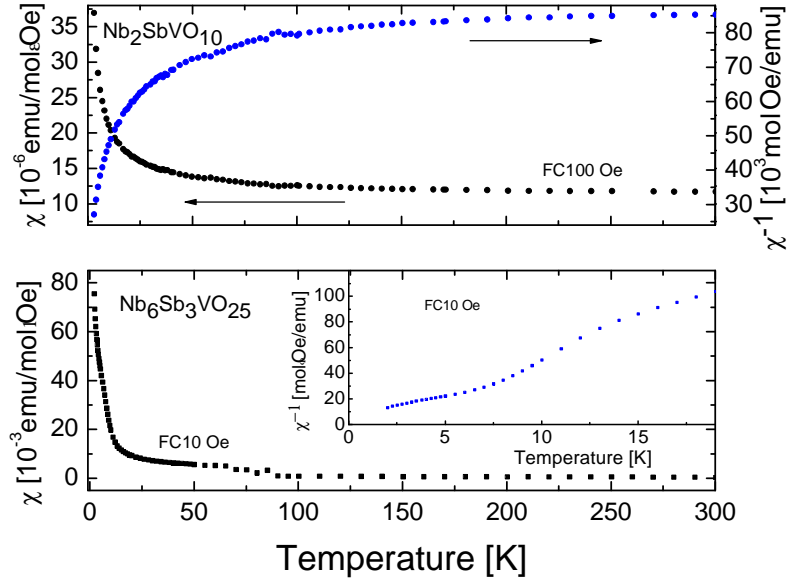


Fig. 1. Temperature dependence of dc magnetic susceptibilities  $\chi$  (right axes) and reciprocal susceptibilities  $\chi^{-1}$  (top panel – left axes and bottom panel – inset) of both compounds

Isothermal magnetisation studies confirmed supposition about a few magnetic components. In the figure 2 isothermal magnetisation  $M(H)$  registered at  $T = 2, 10, 60, 290$  K are shown. It could be satisfactory fitted by the function containing two Brillouin functions for paramagnetic systems of  $S = 1/2$  and  $S > 1/2$  spins and the third term which is linear in magnetic field and temperature dependent:

$$\begin{aligned}
 M(H) = & m_{1/2} \left[ 2 \coth \left( \frac{2\mu_B H}{kT} \right) - \coth \left( \frac{\mu_B H}{kT} \right) \right] + \\
 & + m_{2S+1} \left\{ (2S+1) \coth \left[ \frac{(2S+1)\mu_B H}{kT} \right] - \coth \left( \frac{\mu_B H}{kT} \right) \right\} + P(T) \cdot H.
 \end{aligned} \tag{1}$$

where  $\mu_B$  is Bohr magneton and  $k$  Boltzmann constant. The later term was often used to describe magnetisation of an antiferromagnet below Neel temperature. In case of our compounds it could refer to antiferromagnetic clusters. Magnetizations  $m_{1/2}$  and  $m_{2S+1}$  are saturation magnetizations of the first and the second spin system. The least-squares fitting gave the following values:  $m_{1/2} = 0.0672(8)$  and  $0.23(1) \mu_B/\text{f.u.}$  for  $Nb_2VSbO_{10}$  and  $Nb_6VSb_3O_{25}$ , respectively. These magnetisations are equivalent to 6.7% and 23% of all vanadium ions as  $V^{4+}$  ( $S = 1/2$ ) paramagnetic species. This is a very large difference in magnetisation of both compounds.

For the second term the following values were obtained:  $m_{2S+1} = 0.00070(8) \mu_B/\text{f.u.}$ ,  $2S+1 = 10.5(6)$  for  $Nb_2VSbO_{10}$  and  $m_{2S+1} = 0.0026(5) \mu_B/\text{f.u.}$ ,  $2S+1 = 10(2)$  for  $Nb_6VSb_3O_{25}$ . Thus the second spin system involves paramagnetic clusters with an effective spin  $S \approx 4.5$  but the amount of spins is low, which is equivalent to well below 0.1% of all vanadium ions.

The third term in the above equation can be interpreted as originating due to small antiferromagnetic clusters of magnetic defects, which are very sensitive to thermal motions. The presence of negative magnetisation (visible at high temperatures) is most probably not related to the diamagnetic Meissner effect (superconductivity), but to antiferromagnetic interaction of two magnetic sublattices [1].

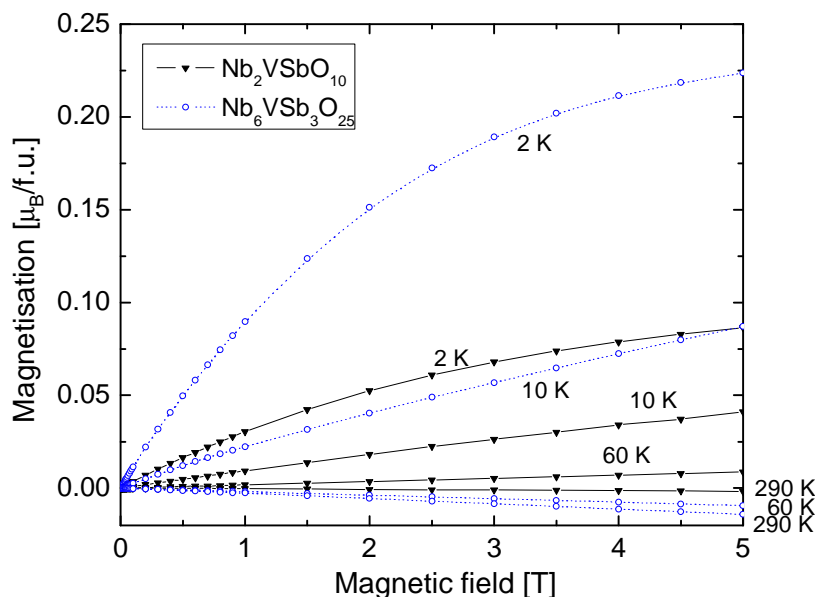


Fig. 2. Comparison of isothermal magnetisation of both samples measured at  $T = 2, 10, 60,$  and  $290$  K

### 3. EPR measurements

In the figure 3 EPR spectra of  $\text{Nb}_2\text{VSbO}_{10}$  and  $\text{Nb}_6\text{VSb}_3\text{O}_{25}$  taken at different temperatures are shown. In case of the former compound the spectrum is more complicated and three components can be perceived. The first one is a rather broad signal close to  $g$ -factor  $g \cong 2$  without a hyperfine structure and it is due to a system of strongly interacting spins. The second component represents partially resolved hyperfine lines and is attributed to isolated vanadium ions in an axial symmetry. The third component is a weak EPR line in magnetic field near 2.8 kG that shifts strongly with temperature changes and it is observed only in a limited temperature range. This line is ascribed to antiferromagnetic clusters. The EPR spectrum of  $\text{Nb}_6\text{VSb}_3\text{O}_{25}$  consists of a single, symmetric and rather strong resonance line in a magnetic field near  $g \approx 2$ , and another weaker signal at  $g \approx 4.3$  that could be due to a forbidden ( $\Delta M_S = \pm 2$ ) transition in a  $\text{V}^{4+} - \text{V}^{4+}$  ( $S=1$ ) pair. The number of magnetic ions estimated from EPR in  $\text{Nb}_2\text{VSbO}_{10}$  and  $\text{Nb}_6\text{VSb}_3\text{O}_{25}$  is equivalent to 5% and 28% of all vanadium ions, respectively. This is roughly consistent with number of paramagnetic ions determined from the magnetisation measurements.

Fitting of the observed spectra with appropriate combination of Lorentzian lineshape lines allowed to obtain EPR spectrum parameters: amplitude, resonance field, line width and another important parameter - EPR integrated intensity  $I_{\text{int}}$ , defined as the product of amplitude and square of the line width. This later quantity is proportional to the magnetic susceptibility (not static, but at microwave frequency) of spin system involved in EPR study and allows comparison with magnetic susceptibility  $\chi$  determined from magnetisation measurements.

In the figure 4 temperature dependence of the EPR integrated intensity is shown for the two compounds. This figure also shows  $I_{\text{int}}^{-1}(T)$  plot and an attempt to fit it with the Curie-Weiss law. It was possible to do this only in limited temperature ranges. For both compounds in the high temperature range,  $T > 100$  K, the Curie-Weiss law fitting gave negative  $T_{\text{CW}}$  ( $-85$  K and  $-122$  K for  $\text{Nb}_2\text{VSbO}_{10}$  and  $\text{Nb}_6\text{VSb}_3\text{O}_{25}$ , respectively), indicating strong antiferro-

magnetic interaction. The strength of this interaction weakens with lowering temperature and below 40 K no interaction is registered in both compounds.

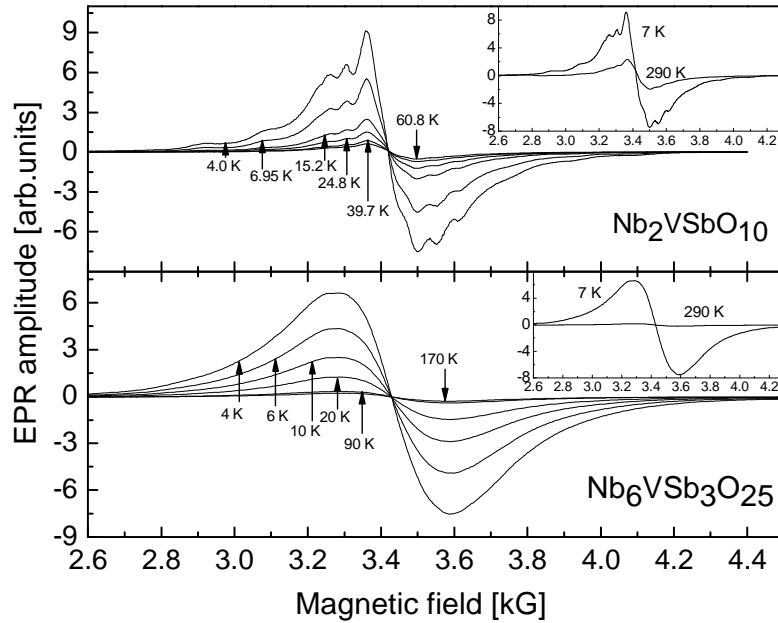


Fig. 3. EPR spectra of both compounds taken at different temperatures. The insets show comparison of registered spectra registered at 7 K and 290 K

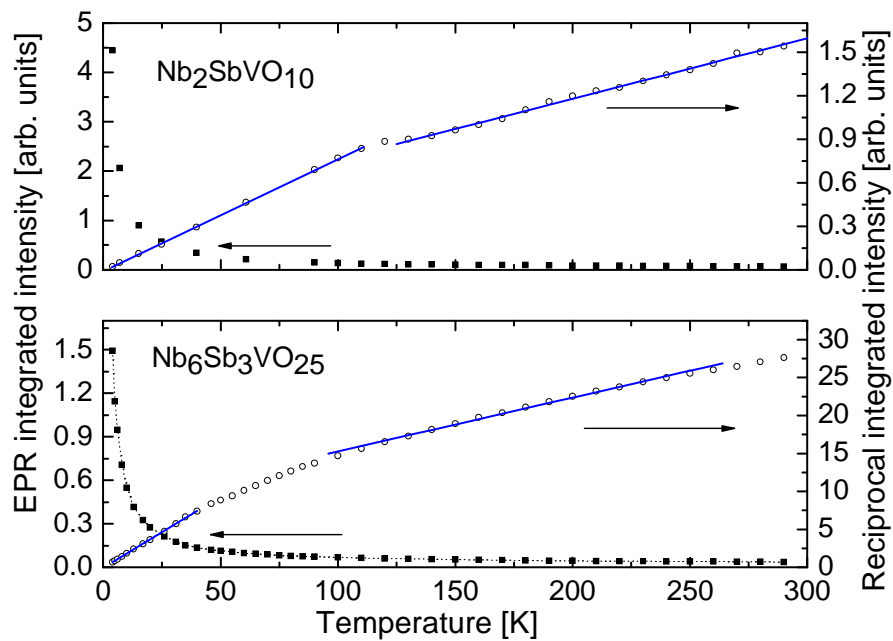


Fig. 4. Temperature dependence of the EPR integrated intensity  $I_{int}(T)$  (left axis) and reciprocal of the integrated intensity  $I_{int}^{-1}(T)$  (right axis) for both compounds. Straight lines are the least-squares fits to the Curie-Weiss law valid only in restricted temperature ranges

#### 4. Conclusions

- It is deduced from EPR and magnetisation measurements that the transfer of electrons from oxygen to the transition metals, changing radically their magnetic state, plays a decisive role in magnetism of both compounds. As the percentage of magnetic ions in  $\text{Nb}_6\text{VSb}_3\text{O}_{25}$  is roughly 4 times higher than in similar  $\text{Nb}_2\text{VSbO}_{10}$  compound, this could be explained by bigger number of oxygens as a source of electrons in the unit cell of the former compound. Also the number of metal ions that could take electrons and turn into magnetic ions is much bigger in  $\text{Nb}_6\text{VSb}_3\text{O}_{25}$ .
- Another important consequence that results from the magnetic studies is the presence of nonhomogeneous distribution of magnetic ions in both compounds. This in turn makes possible formation of different types of clusters and strongly interacting magnetic subsystems. Such distribution of magnetic ions can be explained by assuming that defects are formed on grain boundaries and on other structural imperfections. A large number of defects ensures good catalytic properties so it can be predicted that  $\text{Nb}_6\text{VSb}_3\text{O}_{25}$  compound will be better catalyst than  $\text{Nb}_2\text{VSbO}_{10}$ .

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