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Study of magnetic defects in Nb_2VSbO_{10}

J. Typek[a,*], A. Cyran[a], G. Zolnierkiewicz[a], M. Bobrowska[a], E. Filipek[b], M. Piz[b]

[a] *Institute of Physics, West Pomeranian University of Technology, Szczecin, Al. Piastow 48, 70-311 Szczecin, Poland*
[b] *Department of Inorganic and Analytical Chemistry, West Pomeranian University of Technology, Szczecin, Al. Piastow 42, 71-065 Szczecin, Poland*

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ABSTRACT

Magnetic properties of Nb_2VSbO_{10}, the compound formed in V–Sb–Nb oxide system, were investigated by dc magnetisation measurements using an MPMS-7 SQUID magnetometer and EPR conventional X–band Bruker E 500 spectrometer. Although the nominal valences of the constituting metal ions indicated a diamagnetic material, Nb_2VSbO_{10} displayed rich and interesting magnetic behaviour due to the existence of numerous defects related to oxygen vacancies. Isothermal magnetisation has revealed the presence of three spin subsystems – two different paramagnetic systems and antiferromagnetic spin clusters. EPR spectra showed the presence of three components, involving isolated and interacting V^{4+} ions as well as antiferromagnetic spin clusters. All these magnetic defects are the result of valence changes of metal ions due to charge compensation in the neighborhood of oxygen vacancies, most probably located on grains boundaries.

1. Introduction

Vanadium(V) and niobium(V) oxides as well as compounds and phases formed in reactions between these compounds are effective catalysts for the oxidative dehydrogenation reactions, e.g., for dehydrogenative oxidation of propane to propylene [1]. A large scientific literature indicates that vanadium–antimony oxide catalysts are active in the processes of utilizing such air pollutants as hydrogen sulfide, carbon monoxide, or the oxides of nitrogen [2]. The catalysts based on the system V–Sb–O are also very active and selective in an important reaction of oxidative ammonolysis of propane to acrylonitrile [3]. It is expected that attractive catalytic, electrical, or magnetic properties would emerge in compounds formed from oxides and phases containing niobium, vanadium, and antimony.

Nb_2VSbO_{10} has been identified for the first time in the Nb-Sb-V-O system in 2010 [4]. The indexing of the XRD diffractogram confirmed that it crystallizes in the orthorhombic system with the following unit cell parameters: a=0.328143 nm, b=0.458946 nm, c=1.22476 nm, Z=1 [4]. Nb_2VSbO_{10} has a brownish sandy color and the density 4.67 $g \cdot cm^{-3}$. It is stable in air up to 880 °C and melts incongruently with an accompanying deposition of solid Nb_9VO_{25}[4]. SEM images of Nb_2VSbO_{10} showed the presence of crystals with different sizes - the largest were 3 µm, whereas the smallest did not exceed 0.5 µm in diameter [4]. Electrical resistivity measurements on Nb_2VSbO_{10} ceramics showed an insulating state up to 360 K and above this temperature n-type semiconducting properties with the activation energy of 0.55 eV [5]. Computer-assisted curve fitting procedure of the conductance G *vs.* the applied voltage V showed the relation $G \sim V^{3/4}$. This nonlinearity was recognized as a grain-boundary phenomenon where a barrier to majority charge carriers exists in the depletion layers of the adjacent grains, while the shallow trap levels determine the doping of the grains [5]. Similar current-voltage characteristics were measured in the other compound, $Nb_6VSb_3O_{25}$, synthesized recently in V–Sb–Nb oxide system [6]. Moreover, study of the acid/base and redox catalytic properties of Nb_2VSbO_{10} in comparison with a mechanical mixture of single oxides and a mixture of single and binary oxide (with the same chemical composition) has been reported [7].

Electron paramagnetic resonance (EPR) and dc magnetisation techniques are very often successfully applied in the study of vanadium compounds and they provided many interesting results concerning various magnetic defects [8–19]. Vanadium ion, especially in V^{4+} oxidation state ($3d^1$) is usually very easy to detect by EPR spectroscopy. Also pairs and clusters of vanadium ions are often detected in vanadate compounds and magnetic interactions involving these ions are studied by this technique.

Assuming nominal valence of the four ions forming the Nb_2VSbO_{10} structure: $Nb^{5+}(4d^o)$, $V^{5+}(3d^o)$, $Sb^{5+}(4d^{10})$, $O^{2-}(2p^6)$ it follows that the compound should display only diamagnetic properties. As the defects are expected to be found in the Nb_2VSbO_{10} structure it would be relatively easy to detect them (if they are magnetic) on the diamagnetic background by using dc magnetization and magnetic resonance technique. As frequently the defects are active sites in catalytic processes, the knowledge of the types of defects is crucial for better understanding of mechanisms responsible for catalytic activity. In this

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[*] Corresponding author.
E-mail address: typjan@zut.edu.pl (J. Typek).

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paper such investigation is undertaken to identify all magnetic defects appearing in Nb_2VSbO_{10} compound by using two complementary methods: static dc magnetization and microwave (X-band) EPR spectroscopy.

2. Experimental

Nb_2VSbO_{10} ternary oxide studied in this paper has been obtained by standard solid-state reaction method, according to the following equation [4]:

$Nb_2O_{5(s)}+SbVO_{5(s)}=Nb_2VSbO_{10(s)}$

The following oxides were used in preparation procedures: orthorhombic T–Nb_2O_5 a.p. (Sigma–Aldrich, USA), orthorhombic V_2O_5 a.p. (POCh, Poland) and orthorhombic α-Sb_2O_4 obtained by heating in air of the commercial Sb_2O_3 a.p. (Merck, Germany). Moreover, $SbVO_5$ compound was prepared from oxides V_2O_5 and α-Sb_2O_4 by a conventional method according to the equation: $V_2O_{5(s)}+Sb_2O_{4(s)}+½\ O_{2(g)}=2\ SbVO_{5(s)}$ [20,21]. In the next step of the synthesis a mixture of the composition: 50.0 mol% $SbVO_5$ and 50.0 mol% Nb_2O_5 corresponding to the formula Nb_2VSbO_{10} was homogenized by grinding and heated in air at 600, 620, 650, 675, 690, and 720 °C for 24 h or 48 h until the monophase sample was synthesized [4].

The dc magnetisation measurements were carried out in 2–290 K temperature range using an MPMS-7 SQUID magnetometer and in magnetic fields up to 50 kOe in the zero-field-cooled (ZFC) and field-cooled (FC) modes. Static magnetization of the sample was carried out at T=2,10, 60, and 290 K in magnetic fields up to 50 kOe. EPR study was performed on a conventional X–band (ν=9.4 GHz) Bruker E 500 spectrometer with the 100 kHz magnetic field modulations. The measurements were carried in the 4–290 K temperature range using an Oxford Instrument helium-flow cryostat. The registered spectra were the first derivatives of the absorption curves with respect to the sweeping external magnetic field. EPR spectra were simulated by SimFonia computer program.

3. Results and discussion

3.1. Dc magnetisation measurements

Temperature dependence of dc magnetic susceptibility (defined as χ= *M/H*) is presented in Fig. 1 in three different external magnetic fields (upper panel, left axis). This dependence can be satisfactory described by the sum of two terms: the Curie-Weiss term χ_{cw} and the temperature independent (but magnetic field dependent) χ_0 term:

$$\chi(T) = \chi_{CW} + \chi_0 = \frac{C}{T - T_{CW}} + \chi_0 \tag{1}$$

where C is the Curie constant and T_{CW} is the Curie-Weiss temperature. The top panel in Fig. 1 (right axis) displays temperature dependence of the reciprocal susceptibility $\chi^{-1}(T)$. The value of the Curie constant is slightly field dependent (it increases with magnetic field increase) and changes from C=0.058 emu/(mol·Oe) in H=0.1 kOe to C=0.071 emu/(mol·Oe) in H=5 kOe. Knowledge of the molar Curie constant C (expressed for a mole of substance) allows to calculate the effective magnetic moment (in units of Bohr magnetons):

$$\mu_{eff} = \sqrt{\frac{3k_B C}{N_A \mu_B^2}} \cong 2.\ 828\sqrt{C} \tag{2}$$

where k_B is Boltzmann constant, N_A is Avogadro constant, and μ_B Bohr magneton [22]. The effective magnetic moment of the formula unit calculated from Eq. (2) is in the range of 0.68 – 0.75 μ_B. It is much smaller than 1.73 μ_B for S=1/2 spin because the majority of vanadium ions are expected to be non-magnetic in this compound. The value of the Curie-Weiss temperature decreases with magnetic field increase, changing from T_{CW}=−1.6 K in H=0.1 kOe to −2.5 K in magnetic field 5 kOe. The negative sign of T_{CW} indicates weak effective antiferromagnetic (AFM) interaction in the spin system. Also the value of the temperature independent term χ_0 decreases with magnetic field increase: it changes from 0.0059 emu/(mol·Oe) in H=0.1–0.0053 emu/(mol·Oe) in H=5 kOe. In Fig. 1 the bottom panel shows the temperature dependence of the product of susceptibility and temperature. This product decreases strongly with temperature decrease and most of this decrease is caused by the temperature independent term in Eq. (1).

In Fig. 2 (left panel) the isothermal magnetisation of Nb_2VSbO_{10} compound at four different temperatures (T=2, 10, 60, 290 K) is presented. The experimental points *M(H)* (in units of μ_B/f.u.) were attempted to fit by a single Brillouin function but the result was not acceptable. Only when two Brillion functions, for two different paramagnetic spin systems, and a term proportional to the magnetic field were used the fitting of *M(H)* was satisfactory. Thus the following function was used:

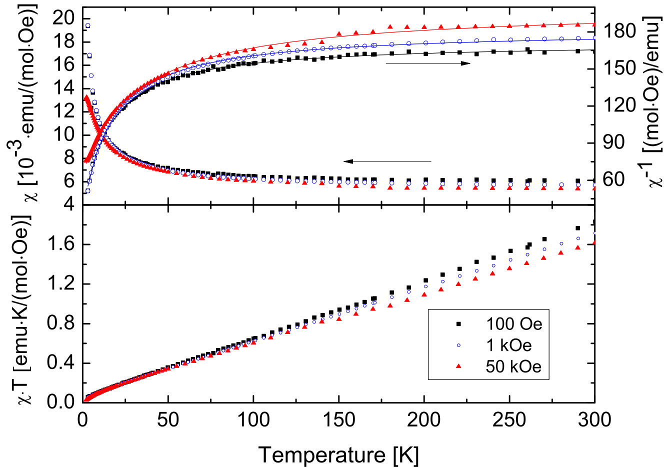

Fig. 1. (Top panel) Temperature dependence of dc magnetic susceptibility (left axis) and reciprocal magnetic dc susceptibility (right axis) measured in ZFC mode in different applied magnetic fields. The solid lines are the least-squares fittings of the experimental points to the reciprocal of Eq. (1). (Bottom panel) Temperature dependence of the product of susceptibility and temperature.

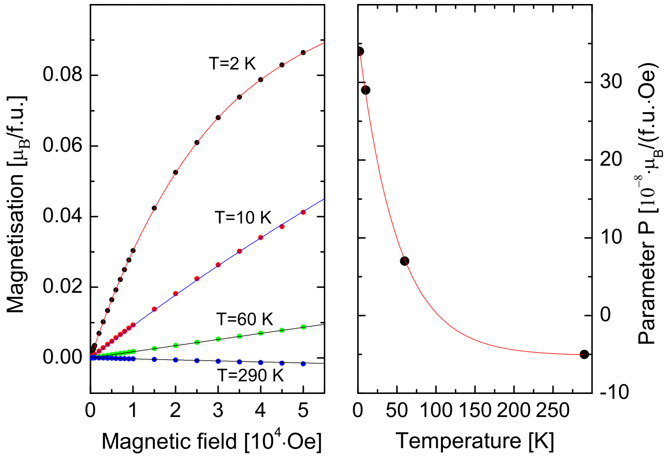

Fig. 2. Left panel: isothermal magnetizations of the Nb_2VSbO_{10} at four different temperatures. The solid lines are the least-squares fittings of the experimental points to Eq. (3). Right panel: temperature dependence of P parameter in Eq. (3). The solid line is the least-squares fitting of the experimental points to Eq. (4).