

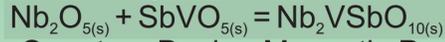
Janusz Typek¹, A. Cyran¹, Grzegorz Zolnierkiewicz¹, Marta Bobrowska¹, M. Piz², Elzbieta Filipek²

¹Institute of Physics, West Pomeranian University of Technology, Szczecin, Al. Piastow 48, 70-311 Szczecin, Poland

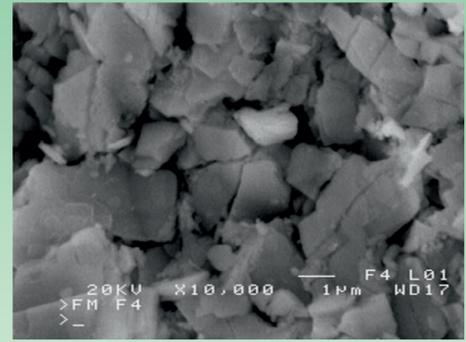
²Department of Inorganic and Analytical Chemistry, West Pomeranian University of Technology, Szczecin, Al. Piastow 42, 71-065 Szczecin, Poland

Experimental

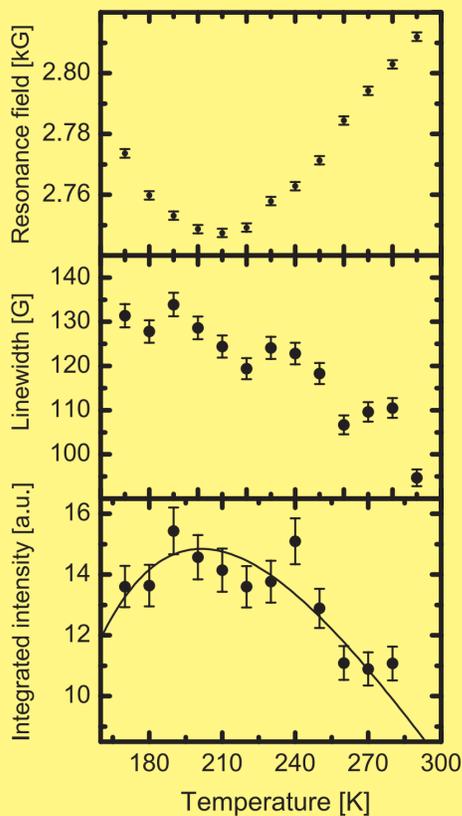
The $\text{Nb}_2\text{VSbO}_{10}$ ternary oxide has been obtained by standard solid-state reaction method, according to the following equation:



Magnetization studies were carried on Quantum Design Magnetic Property Measurements System MPMS XL-7 with a superconducting quantum interference device magnetometer in magnetic fields up to 70 kOe in the zero-field-cooled (ZFC) and field-cooled (FC) modes and in 2–290 K temperature range. 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 ($\nu = 9.4$ 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.



component C



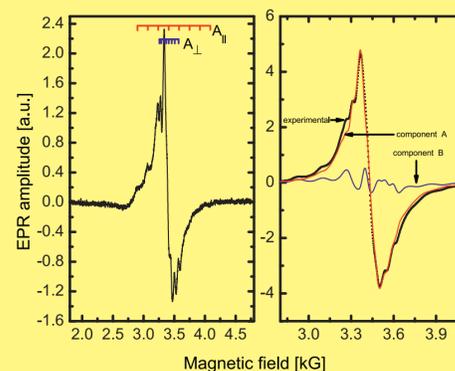
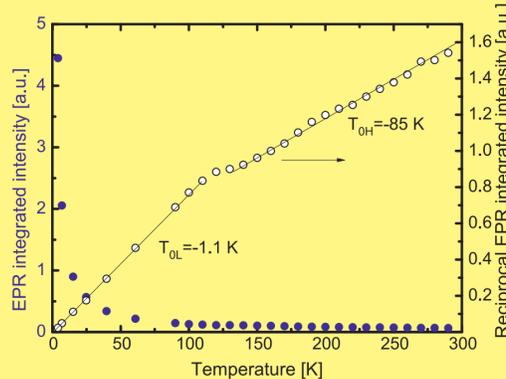
$$I(T) = \frac{A}{T} \exp\left(-\frac{T_0}{T}\right)$$

This type of behaviour suggests that this spectral component might be attributed to the spin clusters.

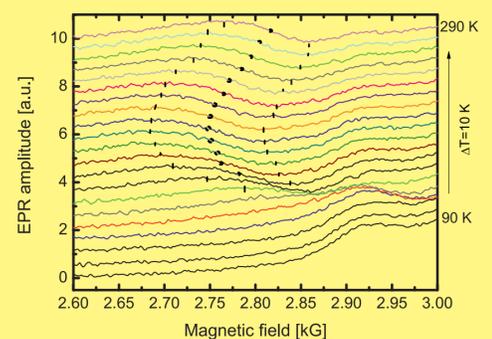
EPR measurements

The registered EPR spectra of $\text{Nb}_2\text{VSbO}_{10}$ can be decomposed on three components (designated as A, B, and C): a rather broad signal in the range of $g \sim 2$ without a hyperfine structure (hfs) (component A), partially resolved hfs lines typical of isolated vanadium ions in an axial symmetry (component B) and a weak line near 2.8 kG that shifts strongly with temperature change and is observed in a limited temperature range (component C). A broad line without hfs (component A) can be simulated with a single powder line arising from $S = \frac{1}{2}$ spins with anisotropic g -factor ($g_{\parallel} = 1.911, g_{\perp} = 1.944$). It could be attributed to a mobile electron hopping along the $\text{V}^{4+}-\text{O}-\text{V}^{5+}$ bond. The hfs could be substantially suppressed or even disappear due to various interactions of electronic spins with their surroundings. One such interaction occurs via a super-exchange through the oxygen bridge of an electron between aliovalent vanadium centres. The component B usually displays two sets of eight lines, partially overlapping, attributed to the interaction of electron spin ($S = \frac{1}{2}$) with nucleus ^{51}V ($I = \frac{7}{2}$, abundance 99.75%).

components A+B

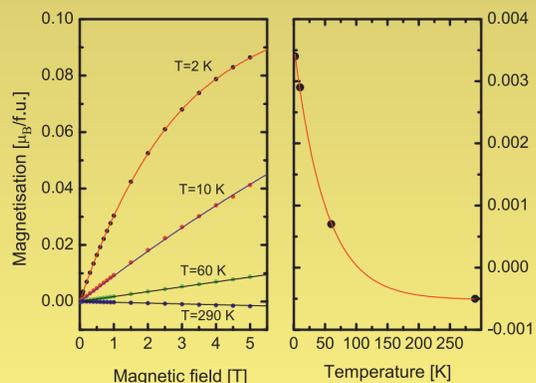
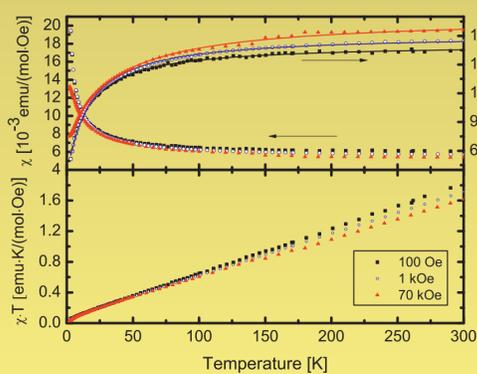


component C



Comparative study at RT of EPR signal intensity (components A+B) with standard $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ sample with a known number of spins was performed to estimate the number of spins in the $\text{Nb}_2\text{VSbO}_{10}$ participating in the resonance. Assuming that vanadium ions in the $\text{Nb}_2\text{VSbO}_{10}$ compound could be only in 4+ (EPR active) or 5+ (EPR inactive) valence states, it was calculated that only 5.2% of the vanadium ions were magnetic and thus in the 4+ valence state.

Dc magnetisation measurements



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

The Curie constant is slightly field dependent (it increases with magnetic field increase). The Curie-Weiss temperature decreases with magnetic field increase. Also the χ_0 decreases with magnetic field increase.

$$M(H) = m_{\frac{1}{2}} \left[2 \coth\left(\frac{2\mu_B H}{kT}\right) - \coth\left(\frac{\mu_B H}{kT}\right) \right] + m_{2S+1} \left[(2S+1) \cdot \coth\left(\frac{(2S+1)\mu_B H}{kT}\right) - \coth\left(\frac{\mu_B H}{kT}\right) \right] + P(T)$$

$$P(T) = P_s + P_0 \exp\left(-\frac{T_0}{T}\right)$$

From: $m_{\frac{1}{2}} = 0.06772(8) \frac{\mu_B}{f.u.}$ follows that 6.7% of vanadium ions are V^{4+}
 $m_{10.5} = 0.00070(8) \frac{\mu_B}{f.u.}$ follows that > 0.1% of vanadium ions are in 2S+1 state

Conclusions

- Two magnetic subsystems of ($S = \frac{1}{2}, S = 4.75$) and AFM clusters follow from magnetization study. EPR shows only $S = \frac{1}{2}$ subsystem.
- Magnetic defects arise from electron transfer from oxygen to metal ions (mostly vanadium).
- Grain boundaries and structural imperfection play an essential role in determining the magnetic properties of $\text{Nb}_2\text{VSbO}_{10}$.