MAGNETIC INVESTIGATIONS OF $Nb_6Sb_3VO_{25}$

Janusz Typek[1], Grzegorz Zolnierkiewicz[1], Marta Bobrowska[1], M. Piz[2], Elzbieta Filipek[2]

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

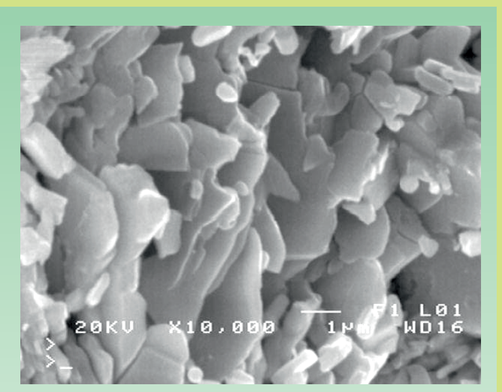
[2]Department of Inorganic and Analytical Chemistry, West Pomeranian University of Technology, Szczecin, Al. Piastow 42, 71-065 Szczecin, Poland

Experimental

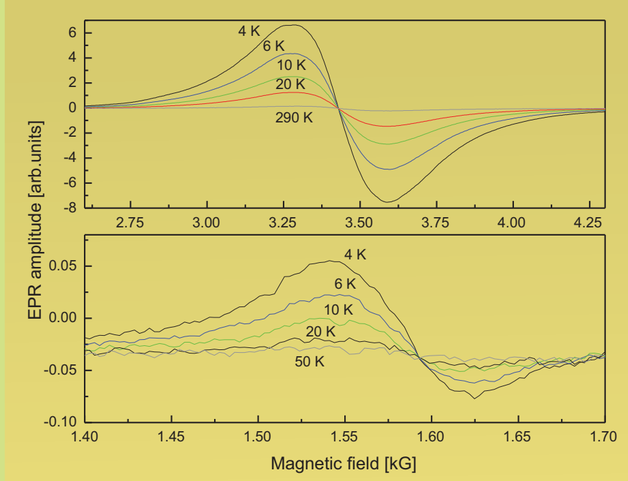
The new compound of the formula $Nb_6VSb_3O_{25}$ in the Nb-V-Sb-O system investigated in this study was obtained by solid state reaction in air:

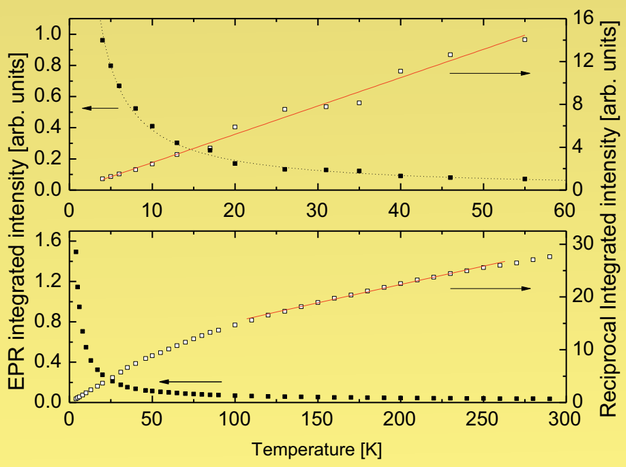
$$V_2O_5 + 6\,T\text{-}Nb_2O_5 + 3\,\alpha\text{-}Sb_2O_4 + 3/2\,O_2 = 2\,Nb_6VSb_3O_{25}$$

Two investigation methods were used: dc SQUID magnetometry and electron paramagnetic resonance (EPR). The magnetization study was carried out on the Quantum Design Magnetic Property Measurements System MPMS XL-7 with a superconducting quantum interference device magnetometer in magnetic fields up to 70 kOe and in the 2–300 K temperature range. The EPR spectra were obtained on a conventional X-band Bruker ELEXSYS E 500 spectrometer in the 4-290 K temperature range by using an Oxford Instruments ESP helium-flow cryostat.

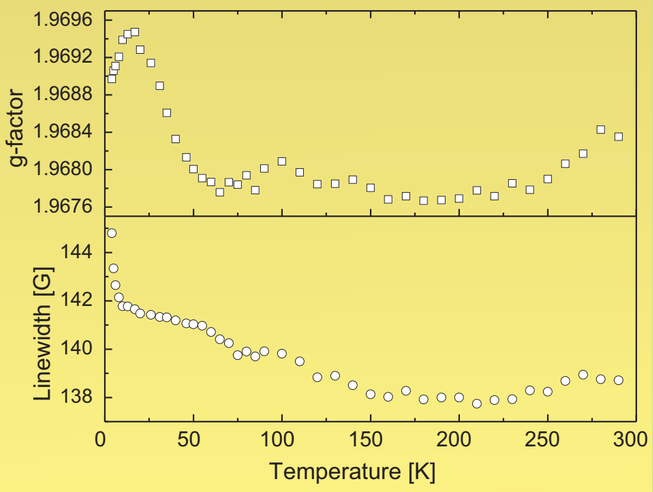


EPR measurements





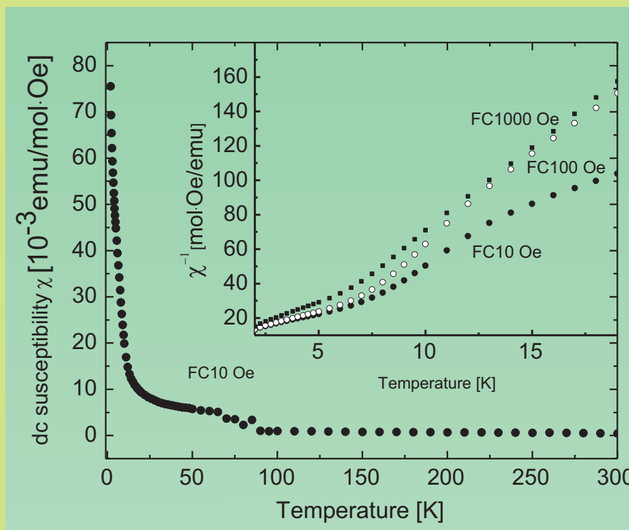
The main feature of the EPR spectrum is a single, symmetric and rather strong resonance line in a magnetic field near g-factor close to 2. The line can be easily fitted with a Lorentzian lineshape indicating that its origin is from an exchange coupled system of S= $\frac{1}{2}$ spins. On cooling from RT the amplitude of the line increases significantly, but its g-factor and linewidth show only small temperature variation in temperature range down to 60 K . An interesting thermal behavior of g-factor and linewidth is observed only in the low temperature range (T<60 K). On further cooling the sample g-factor initially steeply increase to reach a maximum value at ~15 K and then equally significantly decreases on approach to 4 K. This strange behavior might be explained by an effect of emerging and competition of local magnetic field of FM and AFM type during cooling the sample. Similarly, a steep increase of linewidth on cooling the sample below 8 K might be the effect of freezing of the local magnetic field around paramagnetic spins. The vanadium ions in the $Nb_6VSb_3O_{25}$ compound could be only in 4+ (EPR active) or 5+ (EPR inactive) valence states, it was calculated that 28% of the vanadium ions were magnetic and thus in the 4+ valence state. Another EPR line was observed only in the low temperature range. Its amplitude has also increased with temperature decrease, and g factor (close to 4.3) and linewidth didn't show any temperature variation. This EPR signal at g~4.3 could be due to a forbidden ($\Delta M_S=\pm 2$) transition in a pair V4+-V4+ (S=1). The integrated intensity was calculated as the product of line amplitude and squared linewidth. In the high temperature range (100 K<T<250 K), when the Curie-Weiss law is applied, the Curie-Weiss constant T_{CW}= -122 K is obtained, what indicates on a strong AFM interaction between spins in that temperature range.

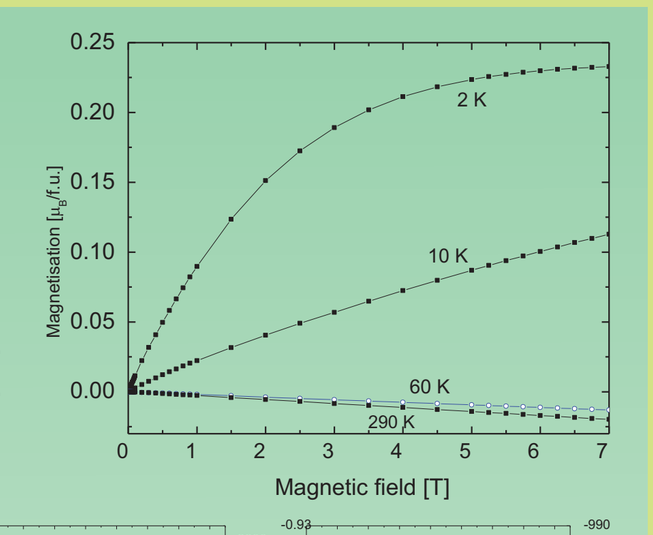


Dc magnetisation measurements

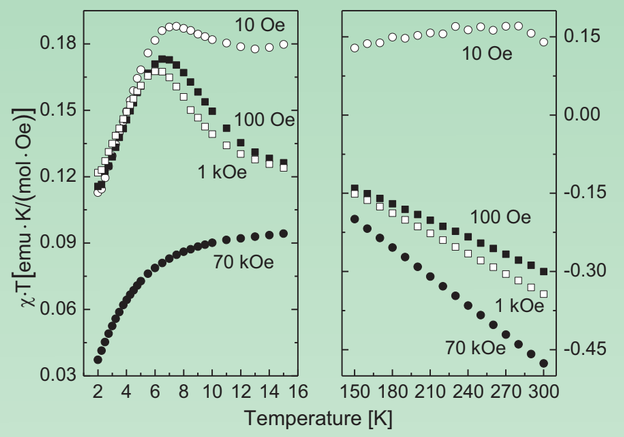
$$\chi(T)=\chi_{CW}+\chi_0=C/(T-T_{CW})+\chi_0$$

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





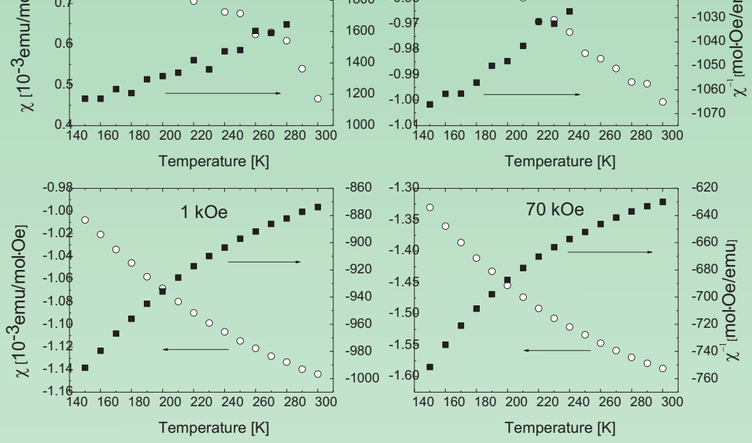
χ(T) dependence indicate on the presence of a few different magnetic entities. The susceptibility is very small near RT, and becomes negative in bigger external magnetic fields. The sign of χ·T curve slope, which indicate on FM (negative) or AFM (positive) interaction depends on the strength of an external magnetic field. In the low temperature range – effective interaction changes sign, from FM at higher temperatures to AFM at lower temperatures.



From: $m_{\frac{1}{2}}=0.23(1)\,\frac{\mu_B}{f.u.}$ follows that 23% of vanadium ions are V^{+4}

$m_{1\,0.(2)}=0.0026(5)\,\frac{\mu_B}{f.u.}$ follows that > 0.3% of vanadium ions are in 2S+1 state

The presence of negative magnetisation is most probably not related to the diamagnetic Meissner effect- the origin is due to AFM interaction of two magnetic sublattices



Conclusions

- Three magnetic subsystem have been identify: 2 paramagnetic (S=$\frac{1}{2}$ and S~4.5) and AFM clusters
- There is a large number of magnetic ions (~ 25% of all vanadium ions)
- There is magnetic competition of FM and AFM interactions
- Magnetic ions congregate on a grain boundaries and structural imperfections
- Charge transfer from oxygen to metal ions is responsible for magnetic properties of $Nb_6Sb_3VO_{25}$