Magnetic resonance study of new compound Nb_2SbVO_{10}

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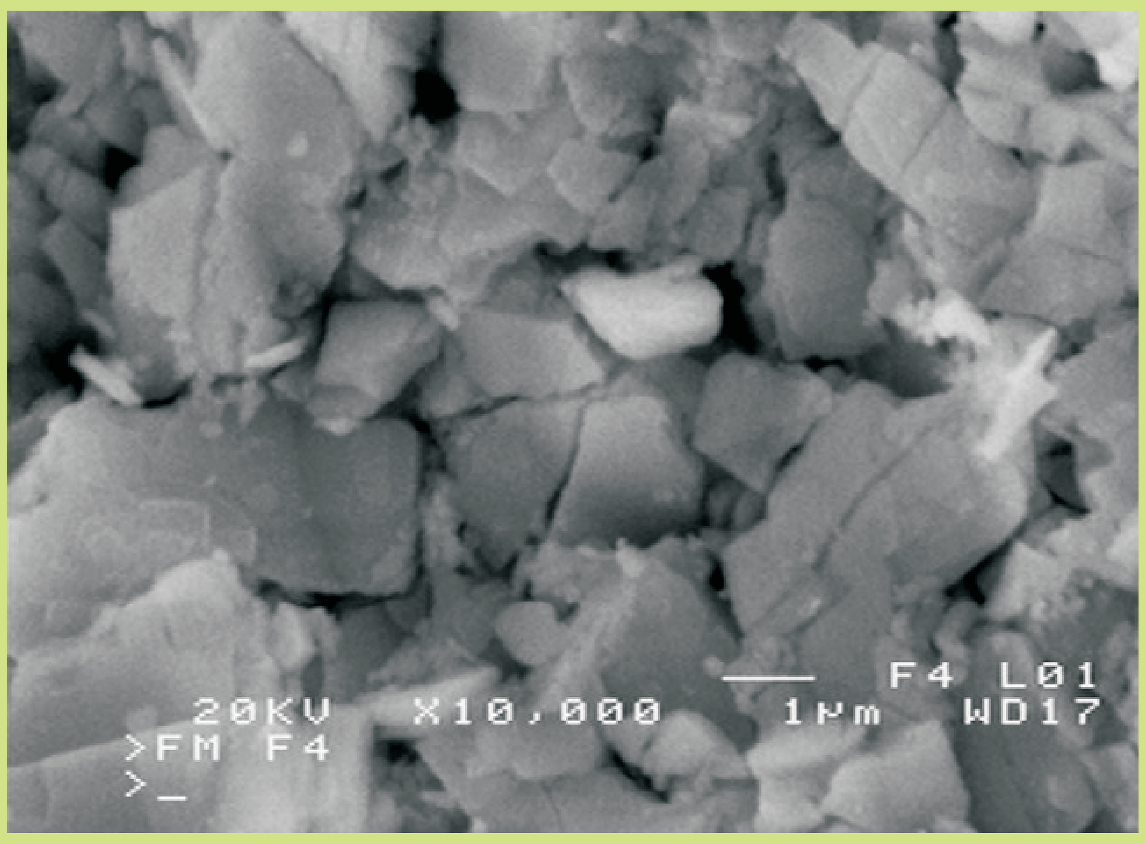
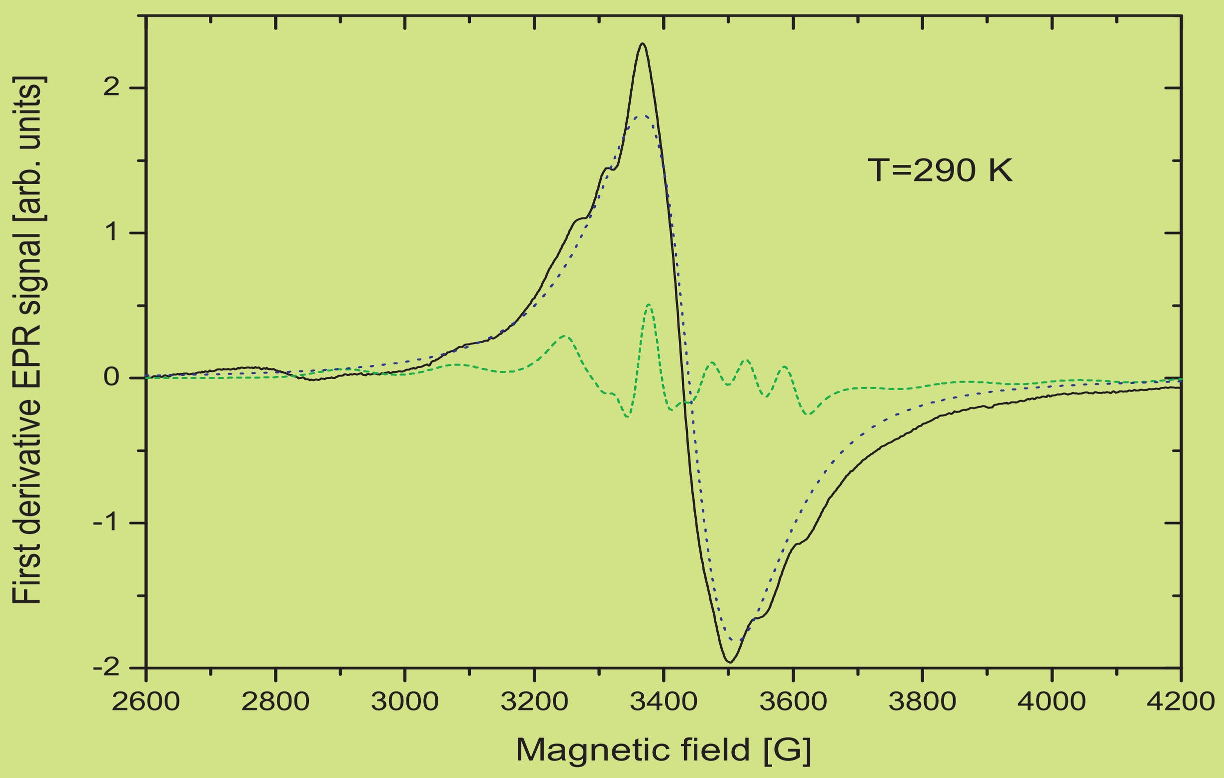
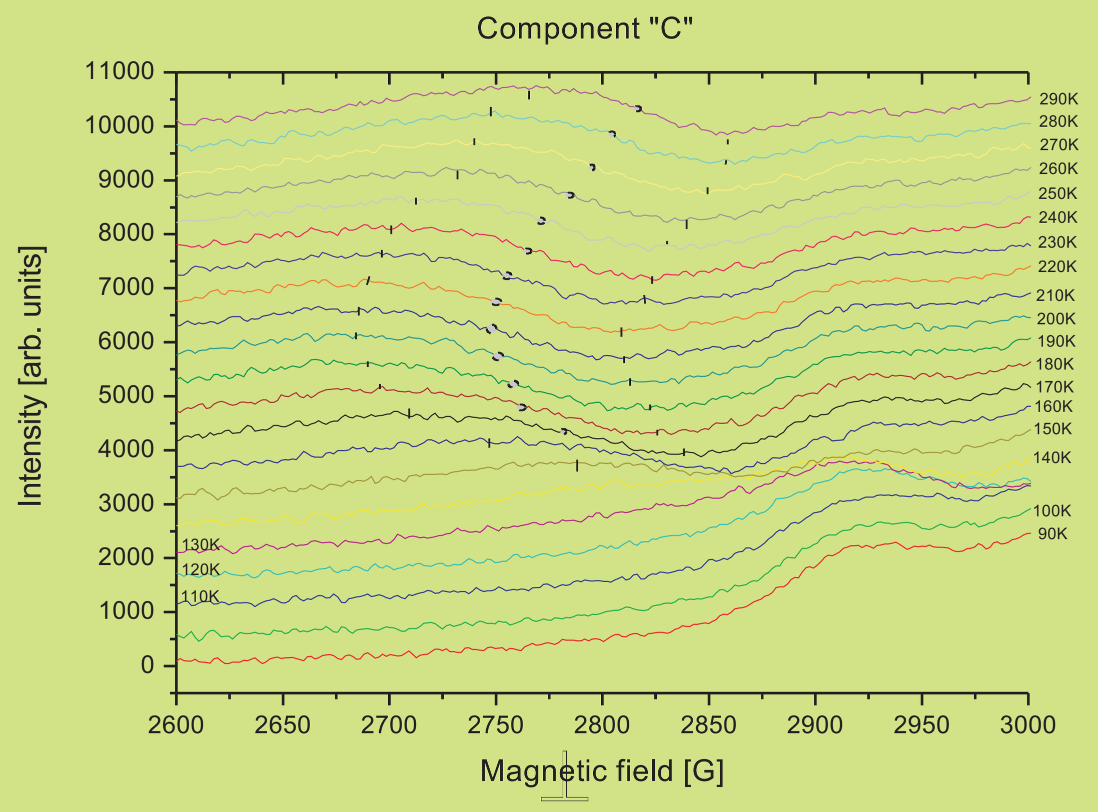
In the last years, the research on multicomponent oxides systems has been intensified in order to obtain new materials of interesting electric, magnetic or catalytic properties. The basic studies on the ternary V_2O_5-Nb_2O_5-Sb_2O_4 system have shown that the oxides formed in the solid state in air contain an unknown compound with the formula Nb_2VSbO_{10}. This compound has been obtained by heating of the mixture $V_2O_5/Sb_2O_4/Nb_2O_5$ (in molar ratio 1:1:2) in air at temperatures up to 750C according to the equation: $V_2O_{5(s)}+2Nb_2O_{5(s)}+Sb_2O_{4(s)}+1/2O_{2(g)}=2Nb_2SbVO_{10(s)}$. The compound Nb_2VSbO_{10} can be also obtained by heating an equimolar mixture of $SbVO_5$ and T-Nb_2O_5 according to the equation: $Nb_2O_{5(s)}+SbVO_{5(s)}= Nb_2SbVO_{10(s)}$. The new compound Nb_2VSbO_{10} is stable in air up to 880°C and next melts incongruently with deposition of solid Nb_9VO_{25}. 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).



SEM picture of Nb_2VSbO_{10} compound.



The observed spectrum of Nb_2VSbO_{10} (continous line) at T=290 K and its two main components: isolated V^{4+} ions (dashed line - component A) and a broad line (dotted line - component B).



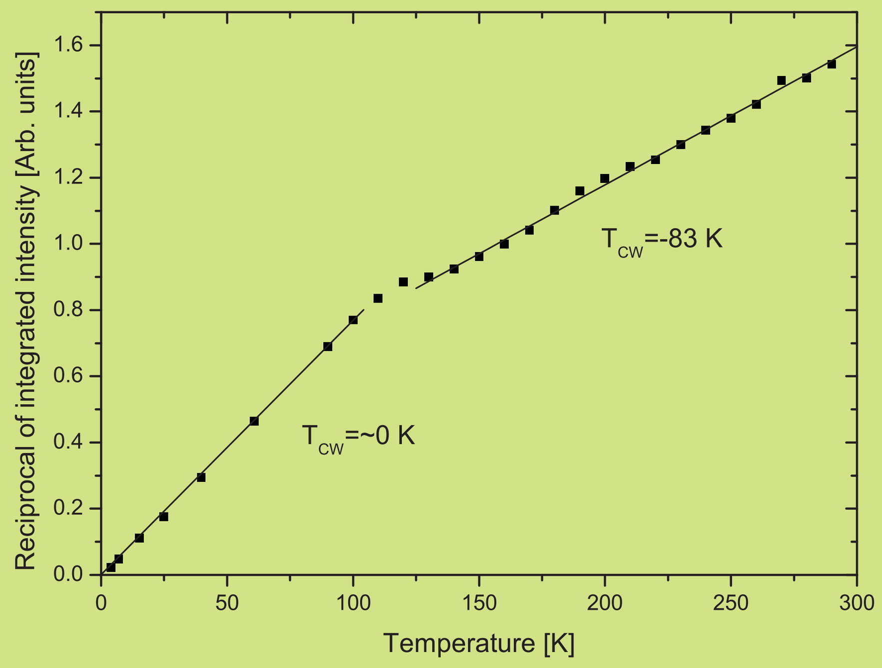
The component C in the EPR spectrum of Nb_2VSbO_{10} at different temperatures.

Electron paramagnetic resonance (EPR) study of Nb_2VSbO_{10} has been carried out on a conventional X-band continuous wave Bruker E 500 equipped with TE_{102} cavity with 100 kHz modulation. The temperature variation studies in the 7-300 K range were performed using an Oxford ESP300 continous flow helium cryostat.

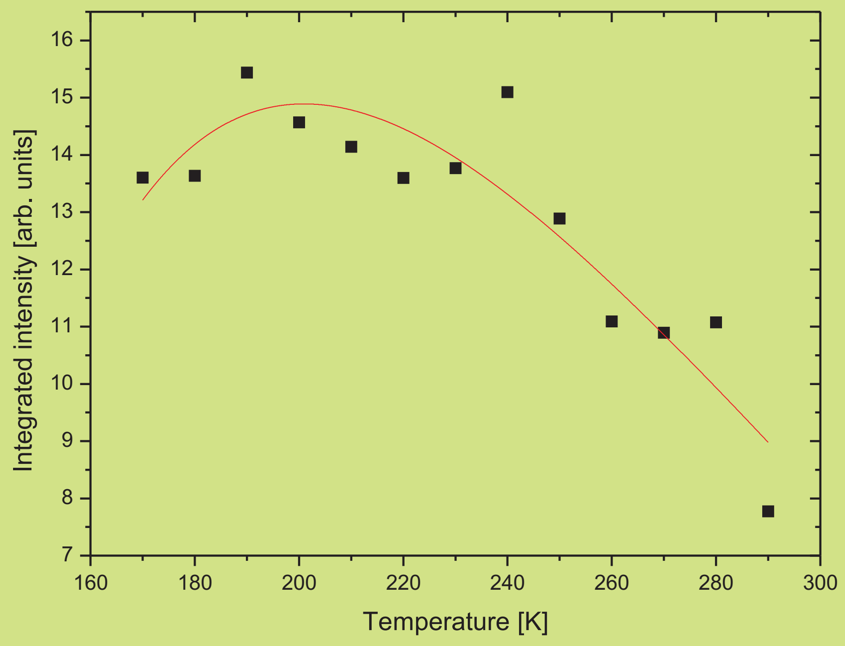
To estimate the number of spins in Nb_2VSbO_{10} sample participating in the resonance a comparative study with standard $VOSO_4•5H_2O$ sample with a known number of spins has been performed. Assuming that vanadium ions in the Nb_2VSbO_{10} compound could be only in 4+ (EPR active) or 5+ (EPR inactive) valence states it was calculated that only 5.2% of vanadium ion are magnetic and thus in 4+ valence state.This concentration of magnetic ions is even smaller than in previously studied $SbVO_5$ compounded. The knowledge of concentration of magnetic ions might be important in estimation of the catalytic activity of the compound as often the minority magnetic ions play a dominant role in such activity.

The EPR spectrum of Nb_2SbVO_{10} in the high temperature range could be decomposed on three components: a broad signal in the range of g≃2 without hyperfine structure (hfs), a partially resolved hfs lines typical of isolated vanadium ions in an axial symmetry and a weak line near 2800 G. The broad line without hfs could be attributed to a mobile electron hopping along the V^{4+}-O-V^{5+} bond. The hfs could be substatailly suppresed or even disappear due to various interactions of electonic spins with their surroundings. One such interaction occurs via the super-exchage through oxygen brigde of an electron between aliovalent vanadium centers. The second component displays usuall two sets of eight lines, partially overlapping, attributed to the interaction of electron spin (S=1/2) with ^{51}V nucleus (I=7/2, abundance 99.75%). This spectrum could be satisfactory described by an axial spin Hamiltonian of the form H = [g B_zS_z + g (B_xS_x + B_yS_y)] + A S_zI_z + A (S_xI_x + S_yI_y), where the symbols have their usual meaning. Fitting the registered spectrum by using the program SimFonia allowed to obtain the following values of the spin Hamiltonian: g =1.907, g =1.947 A =164.6 G, A =43.5 G. These values didn't show any significant temperature dependence. The third component displays a very anisotropic behaviour. It shifts significantly with temperature, reaching the lowest resonance field of 2800 G at 200 K

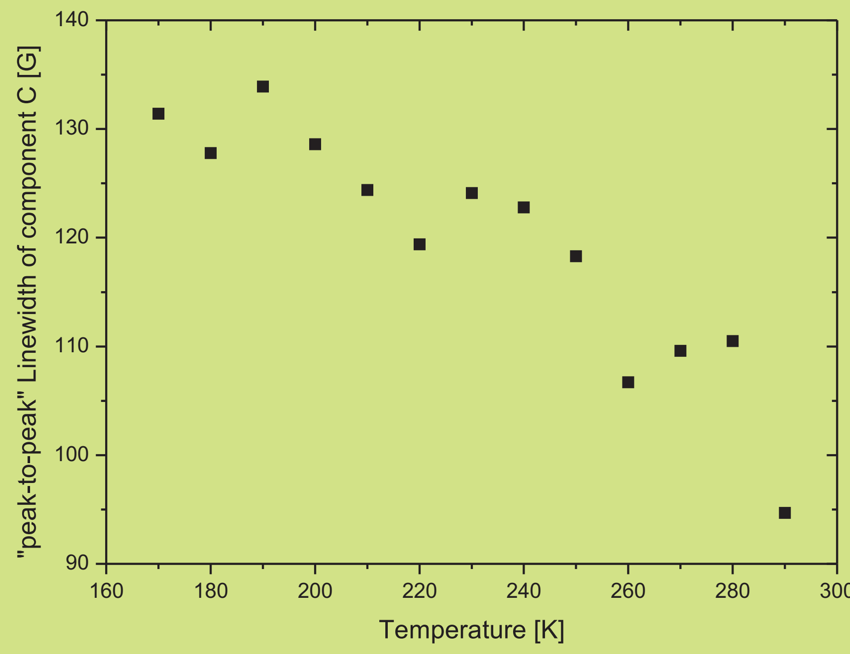
To reveal magnetic interactions in Nb_2SbVO_{10} the temperature dependence of EPR integrated intensity has been studied. In the temperature dependence of reciprocal of integrated intensity two temperature regimes are observed: in high temperature range (T>120 K) this dependence is described by a Curie-Weiss law, $I = C/(T-T_0)$, with T_0 =-82.8 K, while in low temperature EPR range (below 120 K) the Curie law is registered. Negative value of T_0 indicates on an effective antiferromagnetic interaction in the magnetic system of Nb_2SbVO_{10} at high temperature.



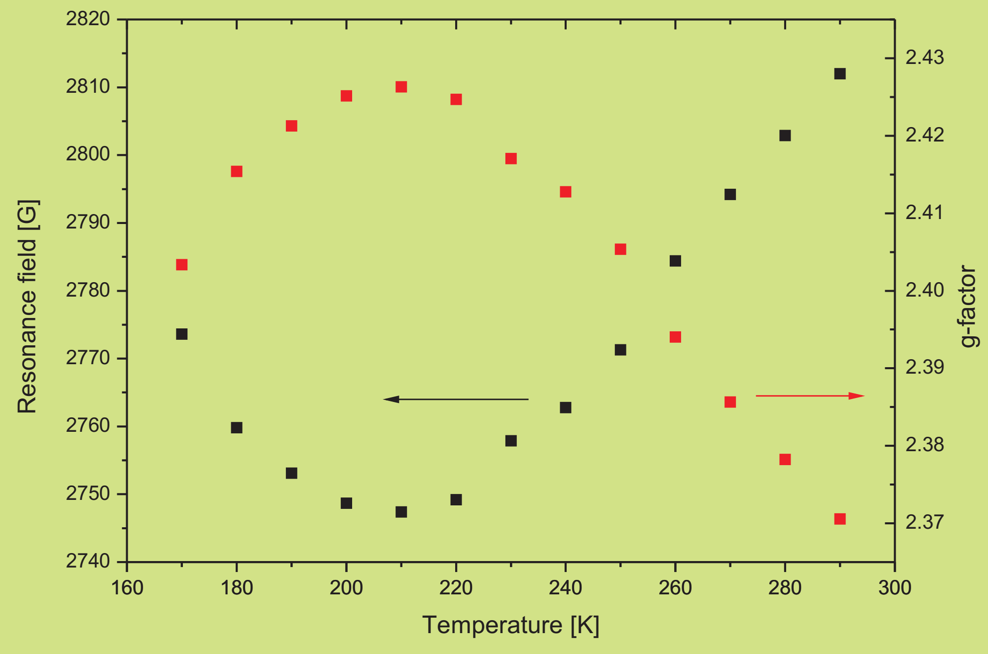
Temperature dependence of the reciprocal integrated intensivity of Nb_2SbVO_{10}. The straight lines are the least squares best fits for the low and high temperature ranges.



Temperature dependence of the integrated intensity of the component C.

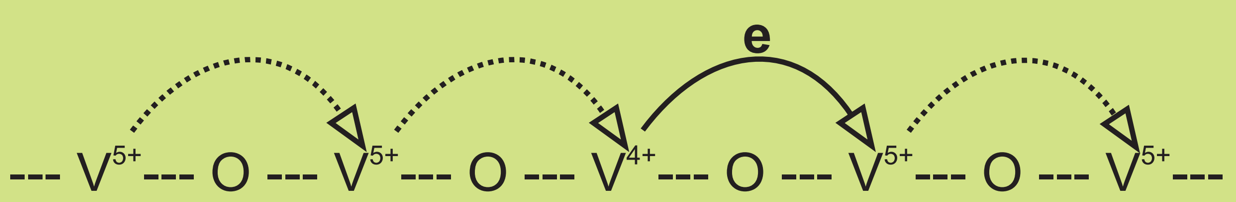


Temperature dependence of peak-to-peak linewidth of the component C.



Temperature dependence of the resonance field (black) and g-factor (red) for the component C.

Model of the component A - isolated V^{4+} ions with hfs.

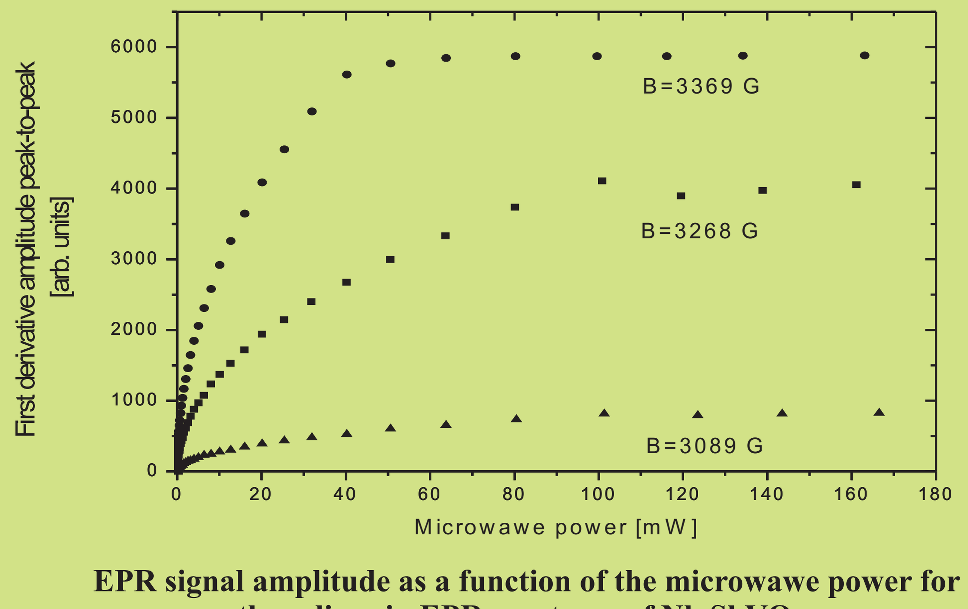


Model of the component B - electron jumping along the vanadium chains.

Model of the component C - antiferromagnetic V^{4+} - V^{4+} dimers

Parameter	Unit	$SbVO_5$	Nb_2VSbO_{10}
$g_{\|\|}$	-	1.9311	1.902
g	-	1.9425	1.93725
g_0	-	1.9387	1.9255
$\Delta g_{\|\|} / \Delta g$	-	1.19	1.542
$\|A_{\|\|}\|$	10^{-4} cm^{-1}	181	147.1
|A |	10^{-4} cm^{-1}	54	38.61
P	10^{-4} cm^{-1}	140	137.1
k	-	0.6244	0.3866
P·k	10^{-4} cm^{-1}	87.4	53.01

Comparison of hfs parameters of two similar compounds: $SbVO_5$ i Nb_2VSbO_{10}.



EPR signal amplitude as a function of the microwawe power for three lines in EPR spectrum of Nb_2SbVO_{10}.