Magnetic resonance study of $Sb_3V_2Mo_3O_{21}$

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Abstract

The $Sb_3V_2Mo_3O_{21}$ compound is formed in the three-component oxide system α-Sb_2O_4-V_2O_5 -MoO_3 from an appropriate amount of these oxides by using the solid-state reaction method. It crystallizes in rhombic system (Z=4) with the following values of unit cell parameters: a=2.0241 nm, b=0.8449 nm, c=0.8169 nm at room temperature. Electron paramagnetic resonance (EPR) study of $Sb_3V_2Mo_3O_{21}$ has been carried out in the 4-290 K temperature range. Comparison with $VOSO_4 \cdot 5H_2O$ intensity standard revealed that only 11.3% of all vanadium ions in $Sb_3V_2Mo_3O_{21}$ are paramagnetic V(IV) species. The temperature dependence of the calculated EPR parameters (g-factor, linewidth, integrated intensity) has been studied and the obtained results are correlated with the proposed magnetic properties of V(IV) single ions and clusters.

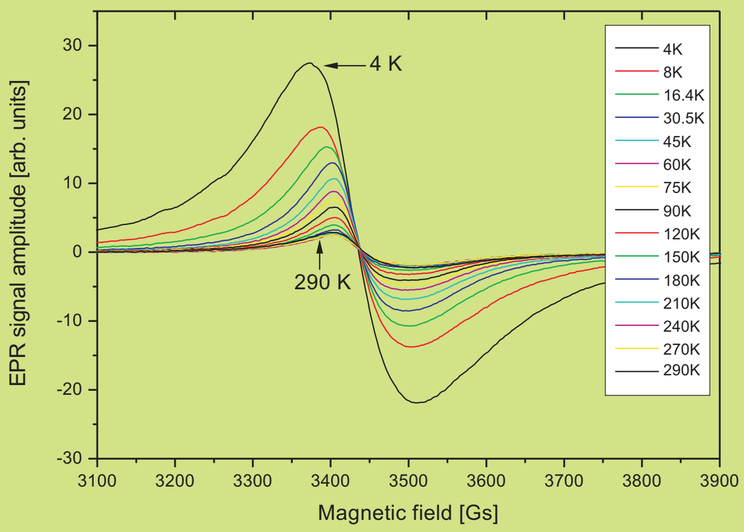

Figure 1. Selection of EPR spectra of $Sb_3V_2Mo_3O_{21}$ powder samples registered at different temperatures in the 4-290 K range.

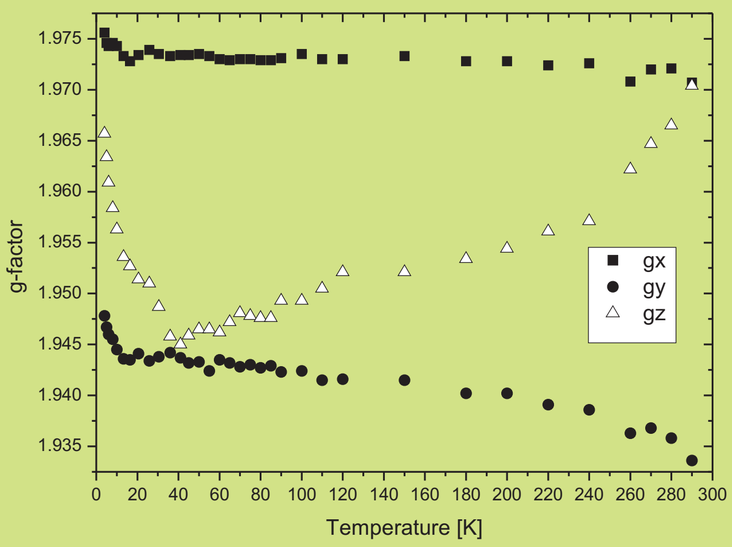

Figure 2. Temperature dependence of the anisotropic g-factors of $Sb_3V_2Mo_3O_{21}$ in the 4-290 K range.

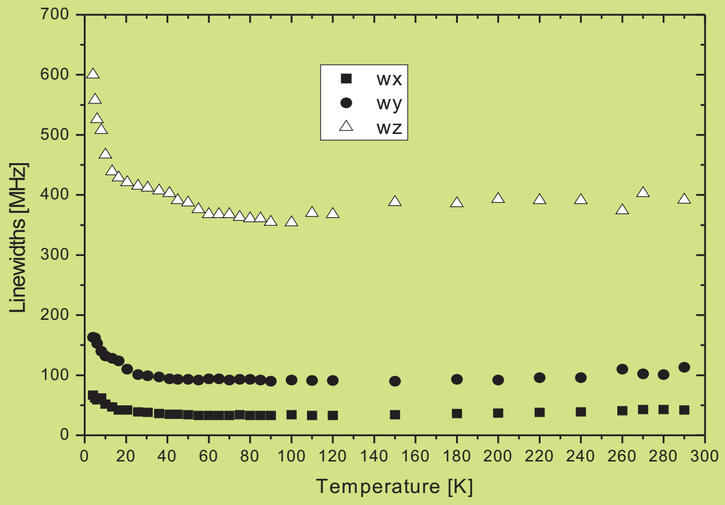

Figure 3. Temperature dependence of the anisotropic linewidths of $Sb_3V_2Mo_3O_{21}$ in the 4-290 K range.

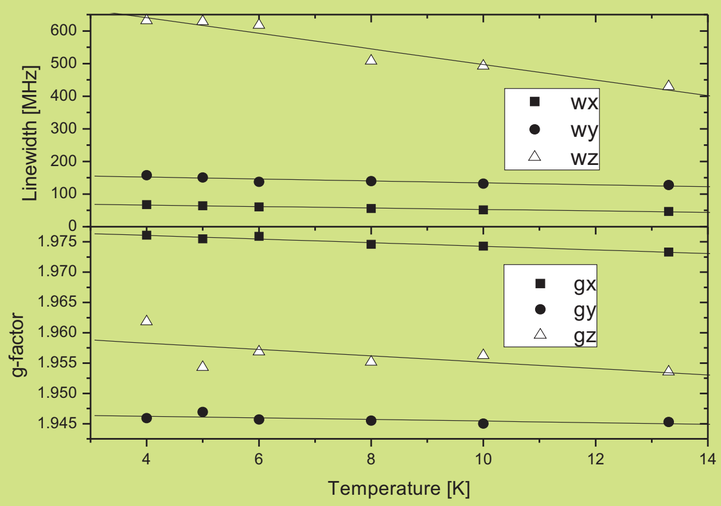

Figure 4. Temperature dependence of the anisotropic linewidths (top panel) and g-factors (bottom panel) in the 4-14 K temperature range.

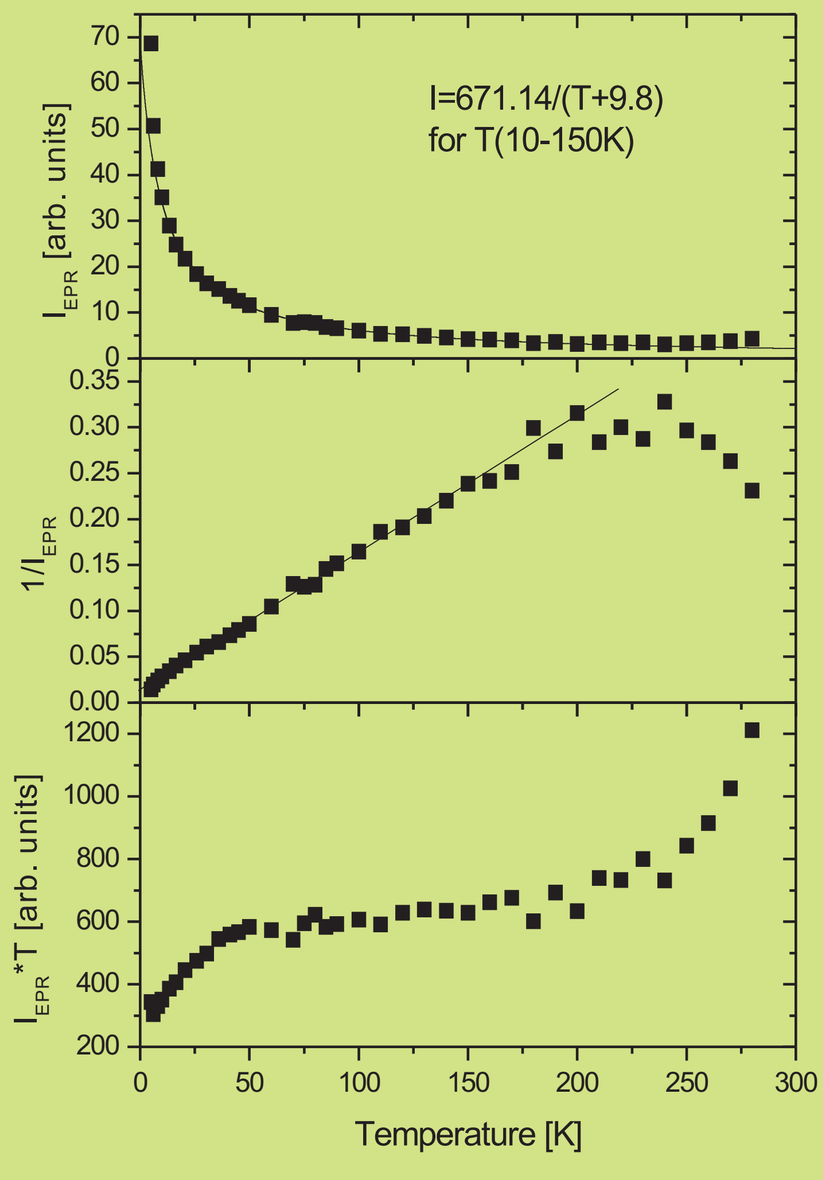

Figure 5. Temperature dependence of the EPR integrated intensity (top panel), reciprocal of integrated intensity (middle panel) and the product of temperature and integrated intensity (bottom panel).

Conclusions

- Most of vanadium in $Sb_3V_2Mo_3O_{21}$ appears as nonmagnetic V^{5+} species (88.7%), only 11.3% as paramagnetic V^{4+} ions and clusters.
- No isolated non-interacting V^{4+} ions are visible in the EPR spectrum of $Sb_3V_2Mo_3O_{21}$. Most observable paramagnetic centers involve strongly interacting V^{4+} ions and vanadium clusters.
- Strong changes of magnetic anisotropy of the spin system with temperature are registered. The *z*-component of *g*-factor displays a peculiar thermal dependence reflecting the symmetry changes o the complex.
- As the magnetic interactions in the spin system of $Sb_3V_2Mo_3O_{21}$ compound are concerned three different temperature ranges could be recognized: the low-temperature range (>10 K), the intermediate temperature range (10-150 K) and the high-temperature range (<270 K). In the low-temperature range an approach to an ordered magnetic state is visible in large shifts of the resonance fields and an abrupt increase of anisotropic linewidths. In the intermediate temperature range an antiferromagnetic interaction between paramagnetic centers is deduced from the temperature dependence of EPR integrated intensity. In the high-temperature range an additional magnetic contribution is registered, probably from antiferromagnically coupled vanadium pairs.