Interplay between structure, transport and magnetism in the frustrated S = 1/2 system In$_2$VO$_5$

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Abstract. Measurements of magnetization, electrical resistivity and nuclear- and electron spin resonance in In$_2$VO$_5$ reveal a remarkable interplay of different degrees of freedom in the zigzag V-O chains (V$^{4+}$, 3d$^1$, $S = 1/2$) which are realized in this material. At high temperatures the d electrons are itinerant and magnetic interactions are ferromagnetic. Below a crossover temperature $T^* \sim 120$K the d states get localized and interact predominantly antiferromagnetically. Though magnetic resonance data clearly indicate the slowing down of the spin-spin correlations by approaching a characteristic temperature $T_{SRG} \sim 20$K the system does not long-range order magnetically. We attribute these peculiar crossover phenomena to the unusual anisotropic thermal contraction of the lattice which controls the localization of the d-states, magnetic exchange and frustration.

1. Introduction
Vanadium oxides often show extraordinary physical properties owing to a complex interplay of spin, charge and lattice degrees of freedom. Here we present results of the magnetization, transport, electron spin (ESR) and nuclear magnetic resonance (NMR) study of the ternary vanadium oxide, In$_2$VO$_5$, where a one dimensional two leg spin-1/2 ladder with sheared legs, the so called zigzag chain, is realized (for details see Ref. [1]).

2. Experimental results and analysis
Powder samples of In$_2$VO$_5$ were prepared according to Ref. [2]. The compound crystallizes in the $Pnma$ space group. The structural elements important for magnetism are distorted oxygen octahedra with the central V$^{4+}$ ion (4d$^1$, $S = 1/2$) which share edges and form a zigzag chain propagating along the b-axis (Fig. 1). $T$-dependent x-ray diffraction measurements reveal a peculiar temperature contraction of the lattice: the c-axis shrinks almost linear by $\sim 0.15\%$ between 300K and 20K. In contrast the a- and b-axes slightly decrease by $\sim 0.05\%$ down to 150K and begin to increase to the same extent by further cooling from a characteristic temperature $T^* \sim 120$K down to 20K.

Electrical resistivity. The electrical resistivity $\rho$ of a ceramic pellet of In$_2$VO$_5$ (Fig. 2) shows a weak $T$-dependence at high temperatures whereas below $\sim 150$K it increases.
Static magnetic properties. The inverse static susceptibility $\chi^{-1}(T)$ of In$_2$VO$_5$ measured in a field of 1 T is shown in Fig. 2, inset. It reveals two linear regimes with different slopes $\partial \chi(T)/\partial T$. The fit to the Curie-Weiss law $\chi(T) = C/(T - \Theta_w)$, where $C$ is the Curie constant and $\Theta_w$ is the Weiss temperature, yields a positive value of $\Theta_w \approx 15\,\text{K}$ for $T > T^* \sim 120\,\text{K}$ and a negative value of $\sim -50\,\text{K}$ for $T < T^*$. The positive sign of $\Theta_w$ indicates ferromagnetic (FM) correlations between vanadium spins whereas the negative sign of $\Theta_w$ implies a net antiferromagnetic (AFM) exchange. Remarkably the sign change of the magnetic interactions occurs at approximately the same crossover temperature $T^*$ where the semiconducting to insulating crossover and the onset of the low temperature increase of the resistivity of In$_2$VO$_5$ at a frequency of 103 MHz was measured at temperatures 4.2 – 200 K. The powder spectrum with unresolved satellites was observed (Fig. 3).

NMR measurements. $^{51}$V NMR in In$_2$VO$_5$ at a frequency of 103 MHz was measured at temperatures 4.2 – 200 K. The powder spectrum with unresolved satellites was observed (Fig. 3). Its shape, the resonance field, and the width remain almost unchanged within the $T$-range of the study. The nuclear longitudinal (spin-lattice) relaxation rate $1/T_1$ shows a sharp enhancement at 20 K (Fig. 3). The strongest channel for the $T_1$ relaxation of $^{51}$V nuclei in In$_2$VO$_5$ is fluctuating electron spins of V$^{4+}$ that exert an effective field at the nuclear spin owing to the on-site hyperfine coupling. The strong enhancement of the nuclear relaxation processes can be related to the critical slowing down of magnetic fluctuations in the electronic subsystem. The peak in the $T$-dependence of $1/T_1$ thus clearly indicates a transition to a magnetically ordered or very slowly fluctuating phase in In$_2$VO$_5$ at $T_{\text{SRO}} \sim 20\,\text{K}$. However, below $T_{\text{SRO}}$, we do not observe a significant broadening and/or splitting and shift of the NMR line indicative of the development of the staggered magnetization in the long-range AFM ordered state. It is therefore plausible that only a short-range (glassy-like) magnetic order (SRO) is realized in In$_2$VO$_5$.

ESR measurements. A multi-frequency high field ESR experiments on In$_2$VO$_5$ have been performed in a frequency range $\nu = 10 – 360\,\text{GHz}$. Surprisingly at all studied frequencies no ESR response from V$^{4+}$ (4$d^1$, $S = 1/2$) ions can be detected above 130 K, i.e. at temperatures larger than $T^* \sim 120\,\text{K}$. Recalling that at $T > T^*$ the resistivity of In$_2$VO$_5$ significantly decreases one can conjecture that vanadium $d$-electrons contribute to conductivity. Owing to a significant spin-orbit coupling of $d$-electrons the momentum scattering of the delocalized $d$-states should
yield a very strong spin-lattice relaxation making ESR signal unobservable. By approaching \( T^* \) from high temperatures a strong ESR signal associated with bulk V\(^{4+}\) spins rapidly emerges. At low and very high frequencies it can be described by a single Lorentzian line profile whereas at 130 GHz < \( \nu \) < 220 GHz the fit requires two Lorentzians: a strong main resonance line and a weak satellite on its left shoulder. The main line shows a linear frequency vs. magnetic field \( H \) dependence \( \nu(H) \) (Fig. 4, main panel). From the slope \( \partial \nu(H) / \partial H \) one obtains a \( g \)-factor amounting to 1.95, the value typical for the average \( g \)-factor of V\(^{4+}\) in a distorted octahedral ligand coordination. The \( \nu(H) \) dependence of the satellite reveals a frequency offset \( \nu_0 \sim 100 \) GHz which corresponds to an energy gap of \( \sim 0.4 \) meV associated with this magnetic excitation. Such a gapped satellite is not expected for a spin-1/2 system but can originate from correlated spin clusters with a total spin \( S_t \geq 1 \). Since at \( T < T^* \) the AFM exchange dominates, short-range dynamic correlations on a frustrated triangular pattern may take place. By considering, for simplicity, an isolated triangle of spins-1/2 AFM coupled by \( J_N \) and \( J_{NN} \) (see Fig. 1 and Sect. 3) one can speculatively assign the satellite to a "forbidden" resonance transition between the \( |S_t = \frac{3}{2}; S_z = \pm \frac{1}{2} \rangle \) ground state of the spin triangle and its high energy \( |S_t = \frac{3}{2}; S_z = \pm \frac{1}{2}; \pm \frac{3}{2} \rangle \) state [3, 4].

The \( T \)-evolution of the ESR spectrum at a selected frequency \( \nu = 270 \) GHz is shown in Fig. 4, inset. Note that at this frequency the satellite peak discussed above merges with the main line. The resonance field \( H_{res} \) is constant whereas the width \( \Delta H \) continuously increases with decreasing \( T \). Below 20 K, an additional resonance mode overlapping with the main line develops and shifts to lower fields (Fig. 4, inset). The appearance of the additional mode corresponds well with the occurrence of the peak in the NMR \( 1/T_1 \) rate at \( T_{SRO} \sim 20 \) K and can be assigned to the resonance response of the SRO regions. The coexistence of two modes indicates a possible intermixing of SRO and paramagnetic regions at \( T < T_{SRO} \).

3. Discussion
Owing to a low symmetry coordination of V\(^{4+}\) the degeneracy of the ground state \( t_{2g} \) set of orbitals is completely removed. The angular overlap model (AOM) calculations identify the \( xz \)
orbital as the ground state orbital which is oriented perpendicular to the $b$-axis (for details see Ref. [1]). The $xz$ orbitals overlap with the $p$-orbitals of the O5 ligands and form V-O5-V bonds that provide AFM exchange paths $J_N$ and $J_{NN}$ for the nearest- (N) and next nearest (NN) neighbor V$^{4+}$ sites, respectively (Fig. 1). The high energy $xy$- and $yz$-orbitals are oriented along the $b$-axis and are expected to overlap significantly in this direction involving O5 $p$-orbitals. The anticipated substantial covalency implies a significant degree of delocalization along the $b$ direction for the electrons promoted into these overlapping molecular orbitals. One can speculate of a formation of a narrow band which would favor an FM polarization of the $d$ electrons. This conjecture could explain an appreciable conductivity, the FM sign of the net exchange and the absence of the ESR signal above a crossover temperature $T^* \sim 120$ K. Indeed, recent band structure calculations reveal significant V-O hybridization and yield a stable FM solution for the room temperature crystal structure of In$_2$VO$_5$ [5]. At lower temperatures the $b$ lattice parameter begin to increase. The width of this hybridized band should therefore decrease which concomitant with its thermal depopulation would cease the FM itinerant behavior and yield the localization of the $d$ electrons. Since the lattice continues to shrink in the $c$-direction the respective shortening of the V-O5 bond parallel to the $c$-axis (dashed line in Fig. 1) should enhance the AFM $J_N$ coupling of $d$-electrons localized on the $xz$ orbitals. Competing $J_N$ and $J_{NN}$ AFM exchange interactions produce magnetic frustration that feasibly drives the system to a disordered or SRO state at low temperatures. In agreement with our results a recent thermodynamical study of In$_2$VO$_5$ in Ref. [6] also suggests the presence of magnetic disorder and frustration and formation of the spin-glass state in this material. This is contrasted by a conjecture of a formation of the global spin-singlet state in In$_2$VO$_5$ put forward recently in Ref. [7]. Obviously the complexity of In$_2$VO$_5$ requires further experimental studies of this material.

4. Summary

In$_2$VO$_5$ is a complex transition-metal oxide which contains zigzag V-O spin-1/2 chains. The experimental study of its static (magnetization) and dynamic (NMR and ESR) magnetic properties complemented by the resistivity measurements reveals a remarkable crossover from the ferromagnetic and conducting regime at high temperatures to the insulating and predominantly antiferromagnetic behavior at low temperatures that eventually results in a frustrated glassy-like magnetic ground state without long-range order. We argue that the occurrence of different regimes in In$_2$VO$_5$ is driven by a peculiar anisotropic thermal contraction of the lattice which yields temperature dependent changes of the overlap integrals and magnetic exchange paths in the V-O chains.

The authors acknowledge stimulating discussions with D. Khomskii. This work was supported by the DFG through SFB 608. The work of E.V. was supported by the German-Russian cooperation project of the DFG (grant No. 436 RUS 113/936/0-1) and by the Russian Foundation for Basic Research through grants No. 08-02-91952-NNIO-a and No. 07-02-01184-a. M.Y. acknowledges the DAAD for support.

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