

Low-Dimensional V-based Complex Oxides: an NMR Study

A.A. Gippius ^{a,1}, E.N. Morozova ^a, D.F. Khozeev ^a, R.V. Spanchenko ^a, E. Kaul ^b,
C. Geibel ^b, A. Rabis ^b, M. Baenitz ^b, F. Steglich ^b

^a *Moscow State University, 119899, Moscow, Russia*

^b *Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, D-01187 Dresden, Germany*

Abstract

We performed ^{31}P and ^{51}V NMR study of low-dimensional isostructural vanadylvanadate $\text{Sr}_2\text{V}_3\text{O}_9$ ($T_{AF} = 5$ K) and vanadylphosphate $\text{Sr}_2\text{VP}_2\text{O}_9$ ($T_{AF} = 2.8$ K). Large negative shift of the whole ^{51}V spectrum in comparison with $\text{Sr}_2\text{VP}_2\text{O}_9$ is an evidence of a strong correlation (coupling) between all three ^{51}V nuclei mediated by electron system. The striking feature of ^{31}P relaxation in $\text{Sr}_2\text{VP}_2\text{O}_9$ is an existence of two characteristic relaxation rates ($R_{1\text{short}}$ and $R_{1\text{long}}$) with more than three orders difference between them. Moreover, the "long" relaxation curve drastically decreases below 15 K. Another result is high value of "short" relaxation which exceeds in two orders of magnitude the ^{51}V relaxation rate in $\text{Sr}_2\text{VP}_2\text{O}_9$. Therefore P-ions are involved in magnetic hyperfine exchange process via the path V-O-P-O-V.

Key words: spin-lattice relaxation; ^{31}P NMR; ^{51}V NMR

1. Introduction

The crystal structure of $\text{Sr}_2\text{V}_3\text{O}_9$ compound contains three types of V site: V^{+4} in VO_6 octahedra forming chains along the c -direction and two V^{+5} in VO_4 tetrahedra which form a connection bridges of two types between VO_6 [1]. In $\text{Sr}_2\text{VP}_2\text{O}_9$ the V^{+5} ions are substituted by P ions which enable us to study the role of non-magnetic cations in magnetic interactions in these low-dimensional V-based oxides [2]. According to magnetic susceptibility and specific heat measurements, $\text{Sr}_2\text{V}_3\text{O}_9$ exhibit the transition to antiferromagnetic (AF) state at $T_{AF} = 5$ K, whereas for $\text{Sr}_2\text{VP}_2\text{O}_9$ the transition is found at $T_{AF} = 2.8$ K [3].

2. Results and discussion

An example of ^{51}V NMR spectra measured in both samples at 295 K and 4 K is shown in Fig.1 and 2. Large negative shift of the whole spectrum (V^{4+} and V^{5+}), in comparison with $\text{Sr}_2\text{VP}_2\text{O}_9$, could be considered as an evidence of a strong correlation (coupling) between all three ^{51}V nuclei mediated by electron system. ^{51}V NMR spectrum at 4 K in $\text{Sr}_2\text{VP}_2\text{O}_9$ has been successfully simulated assuming an existence of one V site and in the presence of following interactions: anisotropic chemical shift; quadrupole 1-st order interaction and indirect ^{51}V - ^{31}P coupling. Nuclear spin-lattice relaxation rate $R_1 = 1/T_1$ of ^{31}P and ^{51}V nuclei in $\text{Sr}_2\text{VP}_2\text{O}_9$ has been measured in the temperature range 4 - 300 K by saturation recovery method using integration of spin-echo in the time domain. The resulting R_1 curves in dependence on temperature are presented in Fig.3. The striking feature of ^{31}P relaxation is an existence of two characteristic relaxation rates ($R_{1\text{short}}$ and $R_{1\text{long}}$) with more than three orders difference between them. Moreover, the "long" relax-

¹ Corresponding author. Present address: Moscow State University, Physics Department, 119899, Moscow, Russia E-mail: morozova@mail.ru

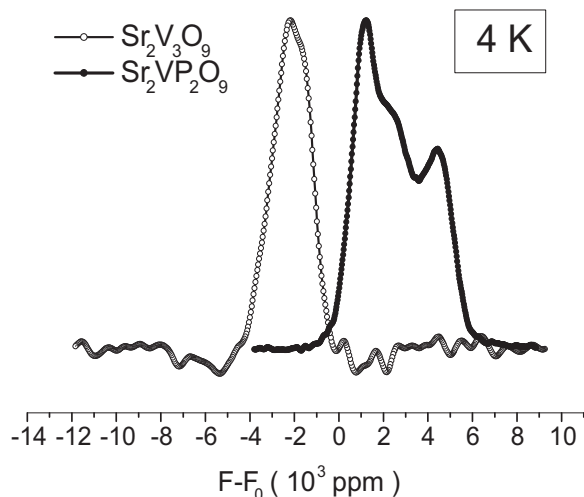


Fig. 1. ^{51}V NMR spectra at 4 K in $\text{Sr}_2\text{V}_3\text{O}_9$ and $\text{Sr}_2\text{VP}_2\text{O}_9$. F_0 is the Larmor frequency of ^{51}V in the magnetic field of 7.014 T [4].

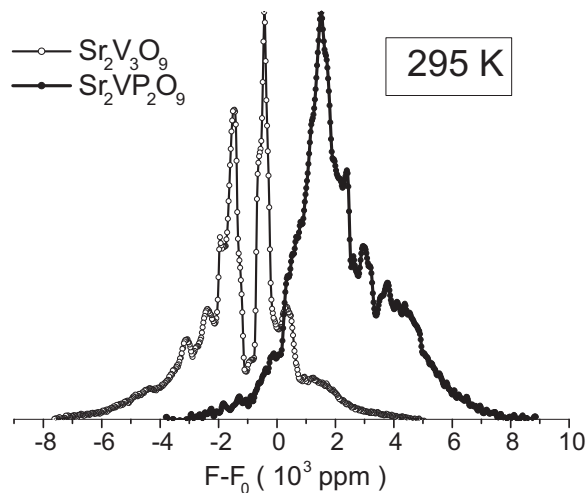


Fig. 2. ^{51}V NMR spectra at 295 K in $\text{Sr}_2\text{V}_3\text{O}_9$ and $\text{Sr}_2\text{VP}_2\text{O}_9$. F_0 is the Larmor frequency of ^{51}V in the magnetic field of 7.014 T [4].

ation curve (bottom curve in Fig.3) drastically falls down below 15 K. This looks like a gap opening in the magnetic excitation spectrum which is, however, not seen in magnetic susceptibility. Taking into account that magnetic susceptibility probes only static uniform magnetic properties one can suppose that such a gap (if it is indeed a gap) should be anisotropic and have nodes in \vec{q} -space. Another surprising aspect of our ^{31}P relaxation data is relatively high value of "short" relaxation which exceeds in two orders of magnitude the ^{51}V relaxation rate in the same $\text{Sr}_2\text{VP}_2\text{O}_9$ compound. This provides a convincing evidence that P-ions are involved in magnetic hyperfine exchange process via the path V-O-P-O-V, which are perpendicular to the chains of

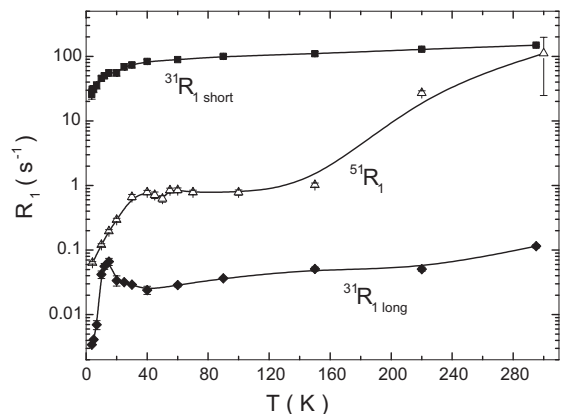


Fig. 3. Temperature dependence of the spin-lattice relaxation rate of ^{31}P and ^{51}V in $\text{Sr}_2\text{VP}_2\text{O}_9$.

VO_6 octahedra. This coincides with the fact that above 40 K ^{31}P "fast" relaxation rate is almost independent on temperature. Similar behavior is observed in 1D Heisenberg spin chain [5]. In the case of more temperature dependent ^{51}V spin-lattice relaxation, one should add in the analysis quadrupolar mechanism which is proportional to T^2 at $T > \theta_D$ and falls down as T^7 at $T < 0.02 \theta_D$, where θ_D is the Debye temperature [6].

3. Conclusion

Our preliminary NMR results show that unique crystal structure of the V-based oxides $\text{Sr}_2\text{V}_3\text{O}_9$ and $\text{Sr}_2\text{VP}_2\text{O}_9$ leads to complicity of magnetic exchange processes reflected in unusual ^{31}P and ^{51}V spin-lattice relaxation behavior.

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