

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

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Abstract

We performed ³¹P and ⁵¹V NMR study of low-dimensional isostructural vanadylvanadate Sr₂V₃O₉ (T_{AF} = 5 K) and vanadylphosphate Sr₂VP₂O₉ (T_{AF} = 2.8 K). Large negative shift of the whole ⁵¹V spectrum in comparison with Sr₂VP₂O₉ is an evidence of a strong correlation (coupling) between all three ⁵¹V nuclei mediated by electron system. The striking feature of ³¹P relaxation in Sr₂VP₂O₉ is an existence of two characteristic relaxation rates (R_{1short} and R_{1long}) 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 ⁵¹V relaxation rate in Sr₂VP₂O₉. Therefore P-ions are involved in magnetic hyperfine exchange process via the path V-O-P-O-V.

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

1. Introduction

The crystal structure of Sr₂V₃O₉ compound contains three types of V site: V⁺⁴ in VO₆ octahedra forming chains along the *c*-direction and two V⁺⁵ in VO₄ tetrahedra which form a connection bridges of two types between VO₆ [1]. In Sr₂VP₂O₉ 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, Sr₂V₃O₉ exhibit the transition to antiferromagnetic (AF) state at T_{AF} = 5 K, whereas for Sr₂VP₂O₉ the transition is found at T_{AF} = 2.8 K [3].

2. Results and discussion

An example of ⁵¹V 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 (V⁴⁺ and V⁵⁺), in comparison with Sr₂VP₂O₉, could be considered as an evidence of a strong correlation (coupling) between all three ⁵¹V nuclei mediated by electron system. ⁵¹V NMR spectrum at 4 K in Sr₂VP₂O₉ 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 ⁵¹V- ³¹P coupling. Nuclear spin-lattice relaxation rate R₁ = 1/T₁ of ³¹P and ⁵¹V nuclei in Sr₂VP₂O₉ 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 R₁ curves in dependence on temperature are presented in Fig.3. The striking feature of ³¹P relaxation is an existence of two characteristic relaxation rates (R_{1short} and R_{1long}) with more than three orders difference between them. Moreover, the "long" relax-

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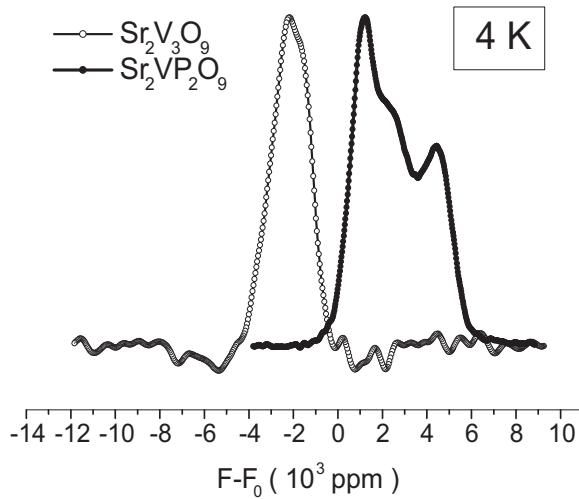


Fig. 1. ^{51}V NMR spectra at 4 K in $\text{Sr}_2\text{V}_3\text{O}_9$ and $\text{Sr}_2\text{VP}_2\text{O}_9$. F_0 is the Larmor frequency of ^{51}V in the magnetic field of 7.014 T [4].

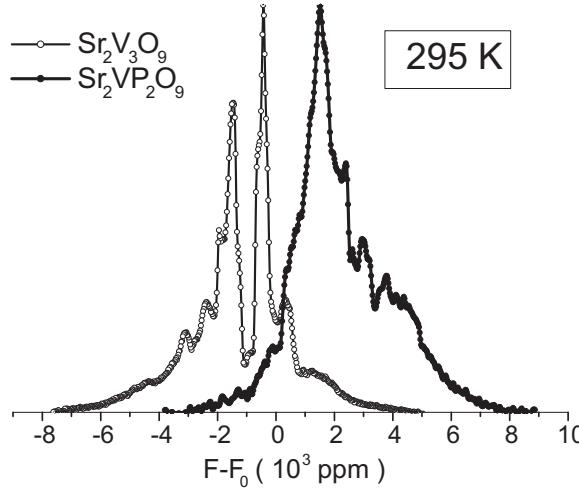


Fig. 2. ^{51}V NMR spectra at 295 K in $\text{Sr}_2\text{V}_3\text{O}_9$ and $\text{Sr}_2\text{VP}_2\text{O}_9$. F_0 is the Larmor frequency of ^{51}V in the magnetic field of 7.014 T [4].

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

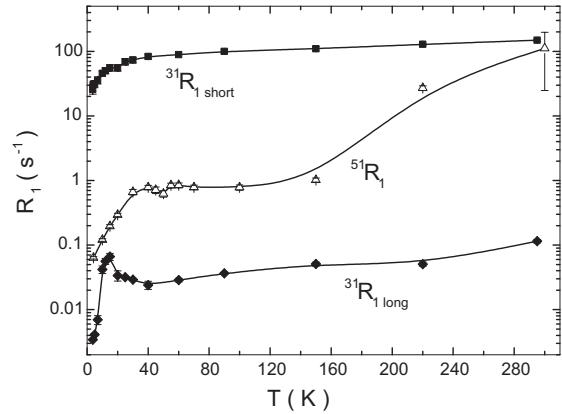


Fig. 3. Temperature dependence of the spin-lattice relaxation rate of ^{31}P and ^{51}V in $\text{Sr}_2\text{VP}_2\text{O}_9$.

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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