MAGNETIZATION AND EPR STUDIES OF A MIXED-VALENCE VANADOGERMANATE

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Introduction

Polyoxovanadates are highly interesting for redox applications in catalysis (e.g. Wacker process, pulp delignification) and materials science (e.g. as cathodes in lithium batteries) [1-3]. Polyoxovanadates containing octahedral hetero groups are much more rare and here we report on the first example of a polyoxovanadate containing an octahedrally coordinated germanium(IV) hetero group. Polyanion $[GeV^{V}_{12}V^{IV}_{2}O_{40}]^{8-}$ (**V_{14}**) is composed of a central $Ge^{IV}O_6$ octahedron which is surrounded by a total of 14 VO_6 octahedra (see Fig. 1). The compact structure of **V_{14}** has D_{4h} symmetry and can be described as an elongated rhombic dodecahedron or a dicapped cuboctahedron.

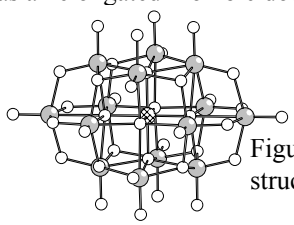

Figure 1. Molecular structure of **V_{14}**.

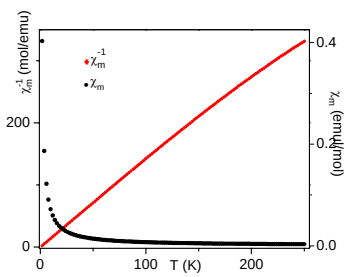

Figure 2. χ_m and $1/\chi_m$ vs T of **V_{14}**.

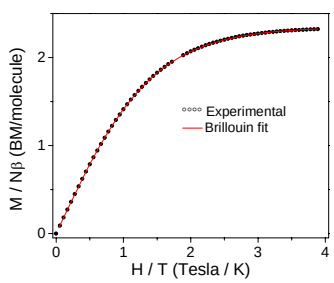

Figure 3. M vs H of **V_{14}**.

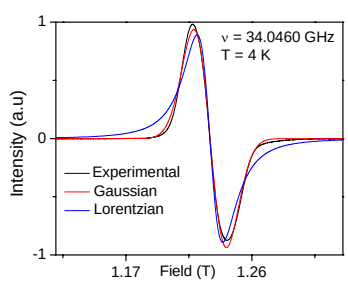

Figure 4. 34 GHz EPR of **V_{14}**.

Experimental

Magnetic susceptibility, magnetization data were collected on Quantum Design MPMS XL SQUID Magnetometer. X-band (~9.5 GHz) and Q-band (~35 GHz) EPR data were collected on Bruker Elexsys 500 at the Department of Chemistry and Biochemistry, FSU.

Results and Discussion

Figure 2 shows the magnetic susceptibility data for **V_{14}**. It is seen that $1/\chi_m$ varies fairly linearly with T over the whole temperature range, as expected for a simple paramagnet. The least-squares-fitting of the $1/\chi_m$ data in the temperature range 1.8 – 150 K using the Curie-Weiss law [$\chi = C / (T-\theta)$], we find that the Curie constant C = 0.710 emu-K/mol and θ = –0.6 ± 0.1 K. Furthermore, substitution of S = ½ and using C = 0.710 emu-K/mol in $C = 2*Ng^2\beta^2S(S+1)/3k$, yields g = 1.946 ± 0.001, in agreement with the EPR value 1.977, with in experimental error. This implies that each V^{IV} ion behaves essentially as a S = ½ ion, well separated from another V^{IV} ion. The isolated behavior of the V^{IV} ions can be further evidenced in magnetization vs field plots (Fig. 3), where the data has been modeled with a Brillouin function for two non-interacting spin ½ ions with g = 1.940 ± 0.001. Both X- (ν ~ 9.4 GHz) and Q-band (ν ~ 34 GHz) show one broad EPR peak (g = 1.977 ± 0.005) at room as well as at low temperatures, which we attribute to the unresolved hyperfine structure arising from ^{51}V (I = 7/2, 99.8% isotopic abundance) nuclei. Our simulations of the lineshape (see Fig. 4) showed that the observed EPR lines at both frequencies and temperatures are predominantly Gaussian, indicating that the spin exchange coupling between the two V^{IV} ions is very small.

Conclusions

Our magnetic susceptibility, magnetization and EPR data complement the X-ray results and confirm the presence of two electrons per molecule [4]. The two V^{IV} ions possessing the spin are very weakly coupled, essentially acting as two well-isolated S = ½ ions. The observed g-value of 1.977 from EPR and magnetic susceptibility measurements is consistent with literature reported value for a V^{IV} ion, suggesting a possible ground state of $3d_{x2-y2}$.

References

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[3] Khenkin, A. M. et. al. *J. Am. Chem. Soc*. **2005**, *127*, 9988.
[4] Kortz, U. et. al. J. Cluster Sci. **2006**, DOI: 10.1007/s10876-006-00484.

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