# $LiV_2O_4$: a heavy-fermion transition metal oxide?

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$LiV_2O_4$ exhibits the fcc normal spinel structure. The formal oxidation state of the vanadium ions 3.5. It is metallic [1] and reveals localized moment magnetism at elevated temperatures [2] with a Curie–Weiss constant of $\theta \approx 35\,K$ and a $g$-value that is consistent with a $V^{4+}(S = \frac{1}{2})$. Substituting Zn for Li induces a spin-glass transition, finally yielding the insulating antiferromagnet $ZnV_2O_4$ [3]. Substituting Ti for V suppresses localized magnetism and yields superconductivity in pure $LiTi_2O_4$ ($T_c \approx 10\,K$) [4]. Guided by NMR and heat capacity experiments it has been concluded that $LiV_2O_4$ is the first HF transition metal oxide.

We performed detailed ESR, magnetic AC and DC susceptibility and heat-capacity experiments in $LiV_2O_4$ and in Zn- and Ti-doped compounds. The probing spin in ESR experiments in metals directly yields information on the local electronic and magnetic properties. The line width at resonance absorption, $\Delta H$, increases linearly as function of temperature, with a slope that is proportional to the density of states at the Fermi energy. In systems with magnetic degrees of freedom in addition to this Korringa broadening the line width is influenced by the dynamic susceptibility. It has been demonstrated that HF systems show enhanced Korringa relaxation, while spin-fluctuation compounds reveal a continuous increase of the line width towards low temperatures [5].

As a representative ESR result, Fig. 1 shows the line width in pure $LiV_2O_4$ and in compounds doped with 30% Zn and 30% Ti, respectively. All compounds investigated reveal an ESR signal characteristic for $V^{4+}(S = \frac{1}{2})$. However, approximately only 0.1‰–1‰ of the vanadium ions contribute to the signal, indicating that we only detect defect states. These V-defects are intimately coupled to the spin fluctuations of the $V^{4+}$ spins as the spin susceptibility closely follows the bulk susceptibility. At low temperatures all three compounds reveal a continuous increase of the line width indicating the importance of spin fluctuations. This increase is not found in HF systems [5]. However, is rather different for the three compounds under investigation. It is strongest in the Zn-doped and weakest in the Ti-doped sample and indicates the continuous suppression of magnetic degrees of freedom when moving from the magnetic Zn compounds to the metallic Ti compounds. From Fig. 1 we conclude the $LiV_2O_4$ is a compound with the spin degrees of freedom playing an important role and being by no means fully compensated by a (possible) Kondo effect.

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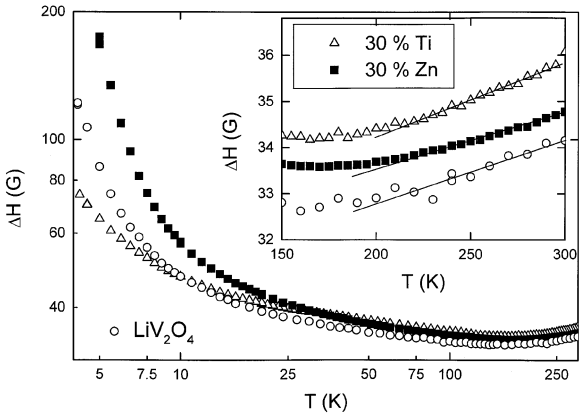


Fig. 1. ESR line width in pure $LiV_2O_4$, $Li_{0.7}Zn_{0.3}V_2O_4$ and $Li_{0.7}Ti_{0.3}V_2O_4$. The inset shows the high-$T$ Korringa behavior.

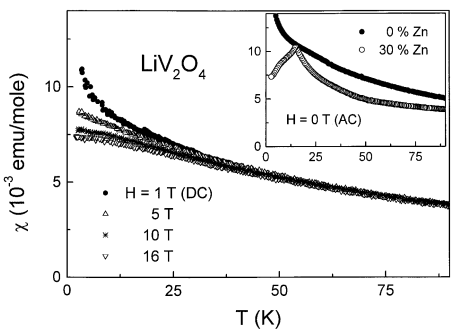


Fig. 2. AC and DC magnetic susceptibilities in $LiV_2O_4$ and $Li_{0.7}$ $Zn_{0.3}V_2O_4$. The AC data is collected at a frequency of $\nu = 3$ kHz with a stimulus of $H_{AC} = 0.2G_{rms}$.

The inset in Fig. 1 shows the high-temperature region of the line width on a linear scale. All three compounds reveal a metallic, Korringa-type of behavior. The slope of $\Delta H(T)$ which is a direct measure of the electronic density of states is lowest for the Zn compound and largest for the Ti compound. However, even for the Ti-doped sample the Korringa slope is almost a factor of 50 lower then in normal metals [5].

The importance of spin fluctuations is also demonstrated in Fig. 2 which shows the temperature dependence of the DC susceptibility in fields up to 16 T. Below 30 K the susceptibility reveals a strong magnetic field dependence. In canonical HF systems the low-temperature susceptibility is only slightly reduced in strong external fields, indicating the formation of band-like heavy quasiparticles with fully compensated magnetic moments. The inset of Fig. 2 shows a comparison of the AC susceptibilities in $LiV_2O_4$ and in $Li_{0.7}Zn_{0.3}V_2O_4$. While the latter compound shows a spin-glass-like cusp at 10 K, the undoped compound reveals a continuously increasing magnetic susceptibility. This could be due to non-Fermi liquid behavior, but it also could indicate a spin–glass transition at lower temperatures.

## References

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