Frustrated 3d Heavy Fermion Spinel LiV$_2$O$_4$

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The 3d spinel compounds AB$_2$O$_4$ (A=Zn,Cd..,B=Cr) and (A=Al,Li..,B=V) exhibit a great variety of exotic electronic ground states [1] which are dominated by two main aspects: Firstly the valence state of the B-3d atom and secondly their location on a geometrically frustrated pyrochlore sublattice consisting of corner-sharing tetrahedrons. For integer valence state like V^{3+} in ACr$_2$O$_4$ the localised d-electrons with spin S=3/2 of Cr may be described by a next neighbor Heisenberg exchange model on the pyrochlore lattice. In this case the geometric frustration property is immediately apparent: The antiferromagnetic exchange energies J$\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ ($J > 0$) for V-V bonds on a tetrahedron cannot be minimized simultaneously for a unique configuration. There is in fact a continuously degenerate manifold of states on each tetrahedron only constrained by $\sum_i \mathbf{S}_i = 0$ which has the same ground state energy. This leads to a macroscopic degeneracy for the ground state of the whole magnetic system. Therefore on a rigid lattice the system would remain magnetically disordered even at the lowest temperatures, i.e., a spin liquid with finite correlation length of spins. Although the paramagnetic Curie Weiss temperature Θ_{CW} that characterizes the strength of magnetic interactions is quite large these compounds remain paramagnetic much below this temperature due to geometric frustration. Finally, however, magnetic order sets in accompanied by lattice distortions that lift the large degeneracy of the exchange energies.

While the effect of frustration is quite apparent for the integer valent local moment spinel compounds it is of much more subtle nature in the mixed valent and metallic spinels such as LiV$_2$O$_4$ and AlV$_2$O$_4$. For itinerant electrons the concept of 'frustration' is not immediately applicable because kinetic energy is described by scalar hopping amplitudes in contrast to the vector product of localised spins in the exchange term. In the former case frustration can only emerge as the result of correlations which leads to enhanced spin fluctuations in the itinerant state. Therefore in the itinerant spinel compounds one may expect an interesting interplay of correlation and frustration effects.

The most dramatic case in this respect is
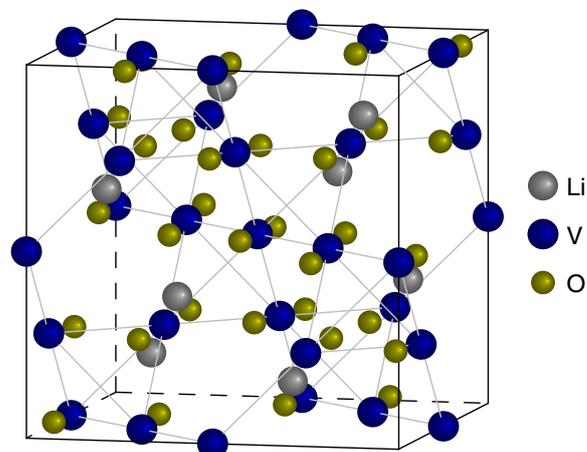
Fig. 1: Crystal structure of LiV$_2$O$_4$. V atoms are located on corner sharing tetrahedrons (thin lines) leading to geometric frustration.

LiV$_2$O$_4$ where this interplay leads to a low temperature heavy fermion metallic behaviour of 3d electrons [2]. Its $V^{3.5+}$ valence state corresponds to a quarter-filling ($n_d = 1.5$ states out of six t_{2g} states are occupied) of d-bands. Therefore a localisation of d-electrons due to Coulomb interactions does not occur and LiV$_2$O$_4$ stays metallic. However the linear specific heat coefficient $\gamma = 0.42 J/molK^2$ observed is in the range of typical f electron heavy fermion metals where the Kondo mechanism is responsible. This has also been proposed for LiV$_2$O$_4$ but application of the Kondo picture with partly localised spins seems not reasonable here. The itinerant nature of the problem was also underlined by the results of neutron diffraction experiments [3, 4]. They showed that the maximum of quasi-static magnetic correlation occurs at a wave vector $|\mathbf{q}| = |\mathbf{Q}_c| \simeq 0.68 \text{ Å}^{-1}$ which is not commensurate with the length of the V-V bonds. Therefore they cannot be interpreted in terms of fluctuations of frustrated localised spins on these bonds. These fundamental observations were a motivation to develop a consistent theory for LiV$_2$O$_4$ starting from the itinerant 3d electron picture including the effect of moderate correlations on the frustrated spinel lattice. The starting point is provided by ab-initio electronic structure calculations in local density approximation [5]. Due to the geometric frustration nearly
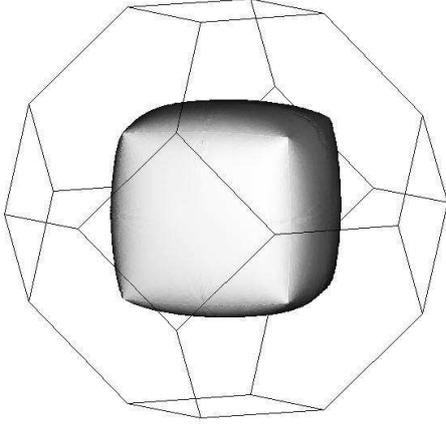
Fig. 2: Surface of critical spin fluctuations (shaded grey) with $|\mathbf{q}| = |\mathbf{Q}_c| \simeq 0.68$ Å^{-1} in the bcc Brillouin zone. On the surface the static spin susceptibilty $\chi(\mathbf{q})$ is maximally enhanced (from Ref. [5]).

Fig. 3: Temperature dependence of reduced inverse critical susceptibility of LiV$_2$O$_4$ on the critical surface in Fig. 2 as obtained from SCR theory [7].

flat bands on the upper unoccupied part of 3d bands appear. They lead to a non-interacting spin response function which exhibits a maximum in an extended shell of the Brillouin zone (Fig. 2). This is a crucial difference to a non-frustrated lattice where the maximum of the spin response occurs only in the narrow vicinity of a well localised wave vector, e.g., around the FM point $\mathbf{q}$=0. Turning on the on-site Coulomb interactions in the former case leads to a critical slowing down of spin fluctuations in the extended shell. This results in a large spin fluctuation contribution to the free energy that explains the observation of the enhanced γ value. A detailed calculation of the momentum dependence of the low temperature spin response gives quantitative agreement with neutron scattering experiments [5].

Under ambient conditions the on-site Coulomb interaction is sub-critical and LiV$_2$O$_4$ is paramagnetic. However application of pressure increases the coupling and enhances the spin fluctuations. Because this happens on the extended isotropic shell no purely magnetic instability occurs and no favorable magnetic ground state can be selected. Instead the compound first undergoes a structural phase transition above 5 GPa leading to a more insulating state which is possibly charge ordered [6]. The precise nature of this insulating high pressure phase and its magnetic ground state is not yet understood.

At ambient pressure the temperature dependence of the spin response [7] can also be understood quantitatively within the spin fluctuation theory [5]

supplemented by the self consistent renormalisation theory (SCR) [8]. At finite temperature the mode-mode coupling of spin fluctuations in SCR approach leads to a gradual decrease of intensity and concomitant increase of line width of the critical modes around $|\mathbf{q}| \simeq |\mathbf{Q}_c|$. Above $T \simeq 30$ K the spin response at $|\mathbf{q}| \simeq |\mathbf{Q}_c|$ and $\mathbf{q} = 0$ become equal. Using the parameter from the T=0 theory and a global mode-mode coupling strength this peculiar T-dependence of the spin response has been fully understood [7].

The quantitative description of the spin fluctuation spectrum contained in the dynamical susceptibility also allows one to understand the heavy fermion behaviour of NMR relaxation rate [9] and resistivity [10] which were explained in Refs. [11, 12]. The NMR relaxation rate $1/T_1T$ due to electronic spin fluctuations may be obtained from the momentum integral over the spin fluctuation spectrum

$$\frac{1}{\omega_n} Im\chi(\mathbf{Q}_c + \tilde{\mathbf{q}}, \omega_n; T) \sim \qquad (1)$$

$$\frac{1}{T_0 T_A} \times \frac{1}{[y_Q(T) + (\tilde{q}^{\parallel}/q_B)^2 + b(\tilde{\mathbf{q}}^{\perp}/q_B)^2]}$$

which is valid close to the critical surface in Fig.2 where $\parallel$ and $\perp$ denote directions with respect to the surface. The constants in Eq. (1) are obtained from the T=0 neutron scattering data [7]. The central quantity of the SCR theory is the reduced inverse susceptibility $y_Q(T) = 1/(2T_A\chi(Q_c, T))$ for spin fluctuations on the critical surface (Fig. 2). It dominates the temperature dependence of all physical quantities described by the spectrum in Eq. (1).
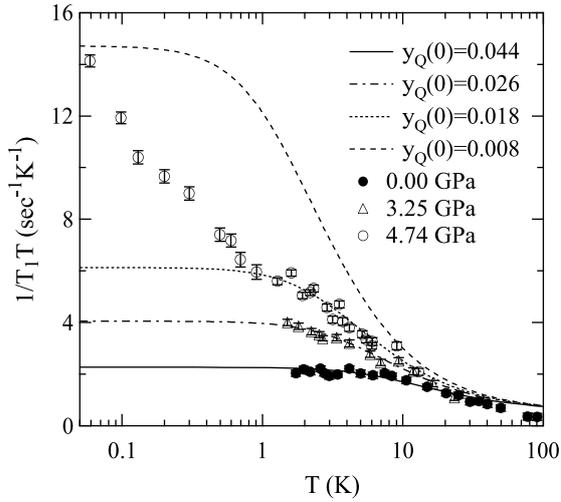
Fig. 4: NMR relaxation rate in LiV_2O_4 for various pressures [11]. Experimental values from Ref. [9]. Korringa regime shifts to lower T for increasing pressure when $y_Q(0) \to 0$ becomes critical.

Fig. 5: Low and high temperature fit to resisitivity (open circles: data from Ref. [10]). Theoretical results from variational Boltzmann approach for scattering from spin fluctuations [12].

The mode-mode coupling inherent in SCR theory means that $y_Q(T)$ is determined by a selfconsistency equation, its solution is shown in Fig. 3 and it corresponds directly to results from neutron scattering [11]. Using this solution the NMR relaxation rate is calculated from Eq. (1) and shown in Fig. 4. The only adjustable parameter is the reduced susceptibility $y_Q(0)$ at T = 0. It increases with applied pressure. For moderate pressure the agreement with theory is excellent, for low temperatures a Korringa relaxation is predicted and observed. On increasing pressure the Korringa regime shrinks and at the highest pressure when LiV_2O_4 approaches the insulating phase the low T behaviour is definitely non-Korringa. This deviation may be due to spin freezing of magnetic defects [11].

The frustration dominated spin fluctuation spectrum in LiV_2O_4 is also at the origin of its anomalous resistivity behaviour. While Fermi liquid dependence $\rho(T) = AT^2$ is found in the heavy fermion regime $T < 2$ K a more modest increase is found for higher temperatures. The Fermi liquid regime shrinks under the application of pressure. This region is equivalent to the one where Korringa type relaxation is observed in NMR. The resisitvity appears via quasiparticle scattering spin fluctuations with a scattering probability $\mathbf{k} \to \mathbf{k}'$ given by

$$
\begin{aligned}
\mathscr{P}^{sf}_{\mathbf{kk'}} &= 3J^2_{sf}f^0_{\mathbf{k}}(1 - f^0_{\mathbf{k'}})[n(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k'}}) + 1] \\
&\quad \times \text{Im}\chi\left(\mathbf{k} - \mathbf{k'}, \varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k'}}\right)
\end{aligned} \tag{2}
$$

It is again essentially determined by the imaginary part of the dynamical spin susceptibility as given in Eq. (1). The scattering, together with the impurity contribution enters the Boltzmann equation for the quasiparticle distribution function. The interference of impurity and critical scattering is essential for obtaining the deviation from Fermi liquid behaviour at elevated temperatures. The variational solution of the Boltzmann equation then provides us with the temperature dependence of the resistivity [12]. The expressions for the resistivity may be evaluated for a high and low temperature fit shown in Fig. 5 with respect to the temperature scale $T^* = 2\pi T_0 y_Q(0) \simeq 16$K (which varies with pressure).

To summarize, the appearance of heavy fermion type behaviour in the spinel LiV_2O_4 has been understood within a SCR calculation of the spin fluctuation spectrum which is based on ab-initio band-structure calculations. The geometric frustration leads to a very peculiar nature of the spectrum with near criticality in an extended shell of momentum space. This explains the basic observations from thermodynamics, neutron scattering, NMR and resistivity measurements through the presence of enhanced spin fluctuations. The transition to the high pressure phase needs to be investigated further.

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