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2001 J. Phys.: Condens. Matter 13 8497

(http://iopscience.iop.org/0953-8984/13/37/307)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 8497–8508 PII: S0953-8984(01)25539-8

Heavy fermions in LiV_2O_4: Kondo compensation versus geometric frustration

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Received 6 June 2001
Published 30 August 2001
Online at stacks.iop.org/JPhysCM/13/8497

Abstract

^{7}Li nuclear magnetic resonance and heat capacity measurements were performed on the metallic spinel LiV_2O_4 down to 30 mK. The temperature dependencies of the linewidth, the Knight shift and the spin–lattice relaxation rate were investigated in the temperature range 30 mK $\leqslant T \leqslant$ 280 K and at applied magnetic fields of 4.6, 10, 44 and 83 kOe. The longitudinal nuclear magnetization was found to relax following a stretched-exponential form with a stretching exponent in the range $0.5 < \beta < 1$. For temperatures $T < 1$ K and at the lowest applied magnetic field of 4.6 kOe, we observe a spin–lattice relaxation rate which slows down exponentially, exhibiting a hindering barrier of the order of 1 K. This excitation energy separates different configurations of a highly degenerate ground state of a completely frustrated magnet.

1. Introduction

LiV_2O_4 has attracted considerable interest since it was reported to show heavy-fermion (HF) formation at low temperatures [1, 2]. On the basis of heat capacity [2], spin–lattice relaxation [2, 3] and neutron scattering results [4], LiV_2O_4 has been treated as a d-based HF system [5], an interpretation which has been corroborated by band-structure calculations [6]. Also in accordance with a heavy-Fermi-liquid description, a temperature dependence of the resistivity $\rho(T) \propto T^2$ has been reported in recent single-crystal work by Urano *et al* for temperatures $T < 2$ K [7]. However, for high temperatures the authors observed no relative maximum in the resistivity $\rho(T)$ at the Kondo temperature T_K. Such a maximum is the fingerprint of coherence phenomena in dense Kondo systems [8] yielding fully compensated magnetic moments at low temperature.

LiV_2O_4 crystallizes in the fcc normal spinel structure and is characterized by vanadium ions in a d^1/d^2 mixed-valence state. In the AB_2O_4 normal spinel structure, the B ions build

a sublattice of corner-sharing tetrahedra while each B ion is octahedrally coordinated by six oxygens. All band-structure calculations [6, 9–11] reveal a t_{2g} level close to the Fermi energy, separated into a lower A_{1g} and a higher E_g orbital. It is emphasized that, in accordance with the Kondo-lattice interpretation, the A_{1g} electrons (d^1, $S = 1/2$) are localized, while the E_g orbitals ($d^{0.5}$) constitute the band states. This interpretation has been derived in close analogy to Kondo-compensated HF systems [6].

An alternative explanation of the rates of spin–lattice relaxation in LiV_2O_4 has been provided within the framework of Moriya's theory [12] of ferromagnetic spin fluctuations. A characteristic temperature $T_0 = 800$ K has been deduced from a high-temperature analysis of the nuclear spin–lattice relaxation rate $1/T_1(T)$ [13, 14]. And indeed, quasielastic neutron scattering studies have provided experimental evidence that at higher temperatures ferromagnetic correlations dominate and the relaxation rates increase linearly with momentum transfer, which is typical of ferromagnetic spin-fluctuation systems [4]. Below 40 K, antiferromagnetic fluctuations dominate and the magnetic relaxation depends only weakly on the momentum transfer.

Assuming an ideal tetrahedral lattice of the V spins and simple antiferromagnetic next-nearest-neighbour interactions, the magnetic order would be highly frustrated. Of course, LiV_2O_4 is rather a good metal and, taking into account the mixed-valence state of the V ions, the situation clearly is much more complicated, allowing no simple predictions about the ground-state properties of this compound. The importance of geometric frustration and the closeness of a ferromagnetic or an antiferromagnetic ground state has been discussed in detail by Eyert *et al* [9]. The close analogy of the magnetic behaviour of LiV_2O_4 to that of other frustrated magnets with spins on tetrahedral lattice sites has been put forward recently by Büttgen *et al* [15]. Taking into account the ideal spinel structure and assuming a low-temperature charge order with two d^1 and two d^2 sites per tetrahedron, Fulde *et al* calculated the ground-state properties for a structure consisting of Heisenberg rings with spin $S = 1/2$ and chains with spin $S = 1$ [16].

To gain insight into the complex ground-state properties of LiV_2O_4, we have performed low-temperature NMR and heat capacity experiments on nominally pure samples which we report on here. In order to check the influence of defect states, different sample qualities have been investigated. The low-temperature NMR linewidth was taken as an indicator of the defect concentration. The heat capacity was measured for 80 mK $\leqslant T \leqslant$ 50 K. For $T \longrightarrow 0$ K, the heat capacity in LiV_2O_4 levels off and follows a $\gamma_0 - \alpha\sqrt{T}$ temperature dependence, which is a hint that LiV_2O_4 is close to a quantum critical point (QCP). From an analysis of the heat capacity results, we can exclude the possibility of static spin-glass (SG) freezing for $T > 100$ mK.

The temperature dependence of the spin–lattice relaxation is reported at different measuring frequencies and external fields from 7.59 MHz/4.6 kOe to 137 MHz/83 kOe, respectively. The temperature dependence of the spin–lattice relaxation rates demonstrates that in LiV_2O_4 there is a slowing down of the spin dynamics towards the lowest temperatures. For zero temperature we speculate regarding a cooperative paramagnet with a dynamic pairing of the spin degrees of freedom, as it is likely to arise in geometrically frustrated systems.

2. Experimental details and results

2.1. Sample characterization and heat capacity

Polycrystalline samples of LiV_2O_4 were prepared by sintering a mixture of powders of $LiVO_3$ and VO with a slight excess of $LiVO_3$ in order to compensate for Li evaporation. Platinum

crucibles were used for reaction of the powders at 750 °C for ten days. From EPR and magnetic susceptibility measurements, we estimated a 0.1% content of V defects. The temperature-dependent specific heat was measured with a quasiadiabatic method in a ^{4}He cryostat for temperatures 4.2 K $\leqslant T \leqslant$ 50 K and in a ^{3}He cryostat for 0.3 K $\leqslant T \leqslant$ 5 K. Measurements to the lowest temperatures of about 80 mK were performed using a relaxation method in a ^{3}He/^{4}He dilution refrigerator. In this case the polycrystalline powder was pressed into thin pellets to reduce the τ_2-effect due to the low thermal conductivity of the samples at very low temperatures.

Heat capacity experiments are presented in figure 1, showing C/T versus $\log T$. Heat capacity data for the isostructural non-magnetic compound $Li_{4/3}Ti_{5/3}O_4$ were taken from reference [2]. Both samples of the pure compound LiV_2O_4 reveal a logarithmic increase for $T \leqslant 10$ K, a plateau below 1 K and a further increase due to nuclear hyperfine contributions. The heat capacity data for sample #2 are shifted to higher values, but reveal a similar temperature dependence. At 1 K, the difference in heat capacity between sample #1 and #2 amounts to almost 20%. Similar discrepancies for nominally pure samples have been reported by Kondo *et al* [2]. In our case these large discrepancies are due to different logarithmic increases of the heat capacity $C(T)/T$ towards low temperatures. It is important to note that we are not able to describe our set of data using a single-ion Kondo model (see later) as was done by Johnston *et al* [17] although we obtain a satisfactory agreement as regards the zero-temperature value of the Sommerfeld coefficient $\gamma(0)$. As sample #1 exhibited the narrowest linewidth in the NMR experiment (see the next section), all further investigations were carried out on sample #1.

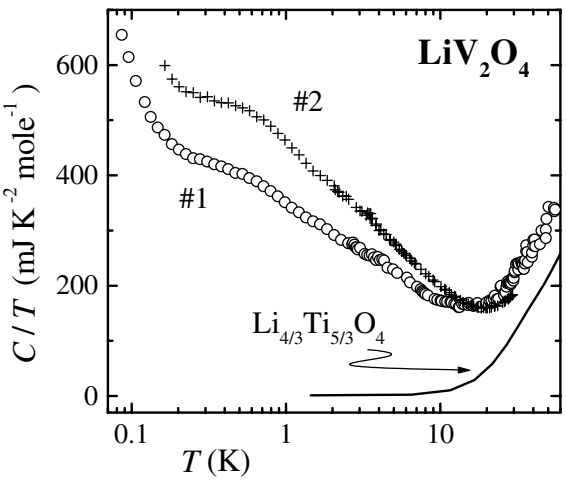

Figure 1. Heat capacity C/T versus $\log T$ for LiV_2O_4 (sample #1 (○) and sample #2 (+)). C/T for $Li_{4/3}Ti_{5/3}O_4$ (solid line) was taken from reference [2] and gives a rough estimate of the phonon contributions.

For a detailed analysis of the electronic heat capacity ΔC of LiV_2O_4 (figure 2) we subtracted the phonon contribution deduced from the non-magnetic reference compound. For a quantitative analysis of the hyperfine term we tried the fit $C/T = 430$ (mJ mol^{-1} K^{-2}) + 0.16 (mJ K mol^{-1})$/T^3$. Here, we took into account a linear Fermi-liquid term and a T^{-2}-term for the high-temperature wing of the Schottky-type hyperfine interaction. The resulting fit for temperatures 80 mK $\leqslant T \leqslant$ 0.35 K is indicated by the dashed line in the inset of figure 2 and gives only a poor agreement. The solid line in the inset of figure 2 represents $C/T = 490$ (mJ mol^{-1} K^{-2}) + 0.13 (mJ K mol^{-1})$/T^3 - 137$ (mJ mol^{-1} K$^{-5/2}$)$\sqrt{T}$

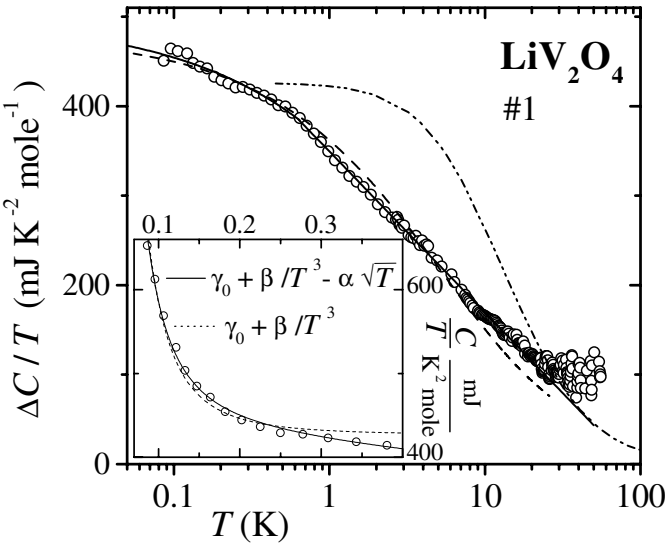

Figure 2. Electronic heat capacity $\Delta C(T)/T$ versus $\log T$ for LiV_2O_4. From the raw data the lattice contribution and the nuclear term (β/T^3) have been subtracted. The bold solid line is the sum of a logarithmic ($T > 0.6$ K) and a square-root temperature dependence ($T \leqslant 0.6$ K). The dashed line indicates a fit using Moriya's spin-fluctuation theory with $T_0 = 26$ K, $y_0 = 0$ and $y_1 = 3.5$. The dashed–dotted line shows the approach using the $S = 1/2$ Kondo model [21] with a Kondo temperature $T_K = 26.4$ K and a Sommerfeld coefficient $\gamma(0) = 426$ mJ mol^{-1} K^{-2} (reference [17]). Inset: the fit to the raw data from figure 1 made in order to estimate the nuclear contribution (see the text).

(80 mK $\leqslant T \leqslant$ 0.6 K) and this fit provides an excellent description of the low-temperature results. In this latter equation we added a square-root behaviour of $C(T)$ in view of the closeness of pure LiV_2O_4 to showing SG order. This behaviour has been theoretically predicted for a spin-glass QCP [18].

For 0.6 K $\leqslant T \leqslant$ 20 K the heat capacity $\Delta C/T$ increases logarithmically, a behaviour that is a hallmark of non-Fermi-liquid (NFL) behaviour and has been observed in many HF systems close to a QCP [19]. For $T < 0.6$ K the heat capacity levels off, following the above-mentioned square-root dependence indicative of a $T \longrightarrow 0$ K SG transition [18] or an antiferromagnetic phase transition at zero temperature [20]. These results are indicated as solid lines in figure 2. Utilizing Moriya's spin-fluctuation theory, $\Delta C/T$ can also be calculated assuming a system close to a magnetic instability [20]. The best fit with the parameters $T_0 = 26$ K, $y_0 = 0$ and $y_1 = 3.5$ is indicated as a dashed line in figure 2. The temperature T_0 characterizes the width of the dynamical spin-fluctuation spectrum and y_0, y_1 are the only two parameters of the reduced inverse susceptibility. Due to the divergence of the temperature dependence of the susceptibility at zero temperature, the parameter $y_0 = 0$ is fixed. Also from this theory, a $\gamma_0 - \alpha\sqrt{T}$ temperature dependence towards $T = 0$ K is expected, but it certainly underestimates the extended $\log T$ regime which is observed in LiV_2O_4 for more than one decade in temperature. Finally, we also indicate the result obtained from a $S = 1/2$ single-impurity Kondo model [21] (the dashed–dotted line in figure 2) which turned out to give only a poor description of $\Delta C/T$ versus T. The only parameter in this model is the Kondo temperature T_K. In the literature, a $S = 1/2$ Kondo model was applied to heat capacity data between 1.2 K and 5 K, yielding Kondo temperatures of $T_K = 27.5$ K and $T_K = 26.4$ K according to Kondo *et al* [2] and Johnston *et al* [17], respectively.

2.2. NMR experiment

The NMR measurements were performed with a phase-coherent pulse spectrometer and spectra were obtained using field sweeps at constant frequencies $\omega_0/2\pi = 7.6$, 17.3, 72.7 and 137 MHz. Cryogenic temperatures were provided by a ^{3}He/^{4}He dilution refrigerator with the NMR resonant circuit inside the mixing chamber. Probing the ^{7}Li nuclei (spin $I = 3/2$, gyromagnetic ratio $\gamma = 16.546$ MHz T^{-1}), we performed measurements of the spin–lattice relaxation rate $1/T_1$. The spectra were collected using a conventional $\pi/2$–τ_D–π spin-echo sequence. The spin–lattice relaxation rate $1/T_1$ was determined from the inversion recovery of the spin-echo intensity. At low temperatures a stretched-exponential relaxation behaviour of the nuclear magnetization was observed as has been reported previously [22].

Figure 3 shows the temperature dependence of the Knight shift and the linewidth at two measuring frequencies in a semi-logarithmic plot. The Knight shift $K(T)$ provides a direct measure of the local static susceptibility. The cusp-like maximum at approximately 30 K indicates the characteristic temperature T^*. The Knight shift is independent of frequency/magnetic field above T^*, but a significant dependence evolves below the temperature of the cusp maximum. For $T < T^*$ the Knight shift decreases approximately logarithmically and levels off at a constant value below 0.3 K which depends on the measuring frequency. Figure 3(b) shows the temperature dependence of the linewidth δ (FWHM), again at two measuring frequencies. For both frequencies, the linewidth continuously increases with decreasing temperature and saturates below 1 K. For the higher frequency and field the increase is significantly enhanced. The linewidth is dominated by an inhomogeneous broadening due to local magnetic fields [3,22]. The constant value at low temperatures signals that the internal fields become frozen and remain constant on the timescale of the experiment. However, below 0.1 K only of 50% of the nuclear spins contribute to the signal as is clearly indicated by the

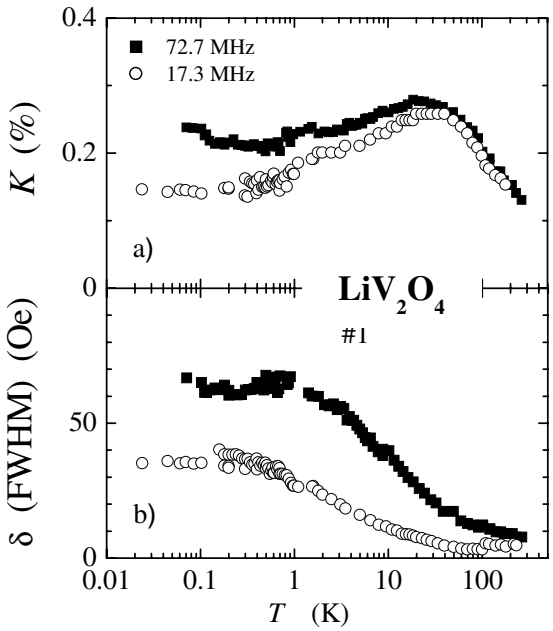

Figure 3. (a) ^{7}Li Knight shift K versus log T for LiV_2O_4 at two measuring frequencies/external fields: (○) 17.3 MHz/10 kOe and (■) 72.7 MHz/44 kOe. (b) ^{7}Li linewidth δ (FWHM) versus log T.

drastic decrease of the NMR intensity towards the lowest temperatures (not shown). It was only the measurements at the lowest frequency and field (7.56 MHz/4.6 kOe) which provided a majority signal of nuclear spins down to temperatures of $T = 100$ mK.

The temperature dependence of the ^{7}Li spin–lattice relaxation rate $1/T_1$ is shown in figure 4(a). Again, the maximum close to 30 K indicates the characteristic temperature T^*. This behaviour nicely resembles the results found by Kondo *et al* [2]. A Korringa-like behaviour has been determined by Kondo *et al* [2] in the temperature range 1.5 K $< T <$ 6 K. In our experiment this Korringa-like behaviour is recovered at higher measuring frequencies and external fields only. The solid line in figure 4(a) indicates a slope of 1, as expected for a pure Korringa relaxation. But it has to be clearly stated that our absolute values of the spin–lattice relaxation rate for all frequencies remain slightly enhanced. This may be due to the fact that we analysed the data assuming a stretched-exponential recovery of the relaxation, i.e. $M(\tau) \propto \exp[-(\tau/T_1)^{\beta}]$, as a pure-exponential fit did not work, especially at temperatures below 1 K [22]. The stretching exponent β was found to vary from $\beta = 1$ at elevated temperatures to $\beta = 0.5$ at low temperatures, independently of the measuring frequencies/external fields.

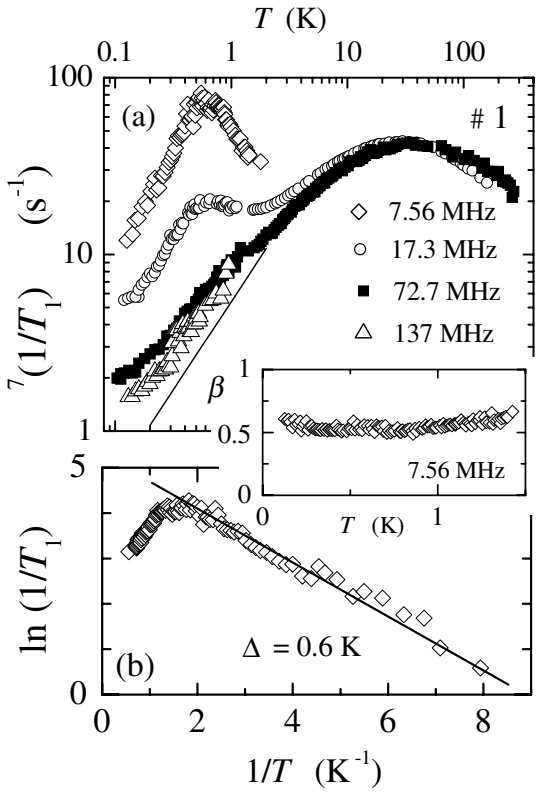

Figure 4. (a) ^{7}Li spin–lattice relaxation rate $\log(1/T_1)$ versus $\log T$ for LiV_2O_4 (#1) measured at different frequencies/external fields: (open diamonds) 7.59 MHz/4.6 kOe, (open circles) 17.3 MHz/10 kOe, (closed squares) 72.7 MHz/44 kOe and (open triangles) 137 MHz/83 kOe. The solid line indicates a Korringa relation $1/T_1T =$ constant. (b) An Arrhenius plot of the spin–lattice relaxation rate $1/T_1$ at 7.59 MHz/4.6 kOe. The solid line represents a fit $1/T_1 \propto \exp(-\Delta/T)$ with $\Delta = 0.6$ K. Inset: the stretching exponent $\beta \approx 0.5$ of the spin–lattice relaxation at 7.59 MHz/4.6 kOe for 126 mK$< T <$ 1.4 K.

Astonishingly, at low measuring frequencies a clear cusp-shaped maximum appears at approximately 0.6 K which becomes suppressed at higher frequencies and higher fields. Below 2 K the anomalous temperature dependence of $1/T_1$ reveals a significant frequency dependence and the nuclear relaxation is strongly enhanced at low frequencies. This behaviour clearly reveals a similar characteristic to the Li nuclear relaxation observed in Li-doped CuO and NiO by Rigamonti and co-workers [23] which has been compared to the spin dynamics in cuprate superconductors. On the basis of this interpretation, the cusp-like anomalies in figure 4(a) below 1 K signal the slowing down of spin fluctuations on a timescale given by the NMR experiments. It is important to note that the spin–lattice relaxation rates $1/T_1$ were obtained from a stretched-exponential behaviour, and for stretching exponents $\beta < 1$ the quantity $1/T_1$ is not a well-defined average rate. However, for all practical purposes we will treat $1/T_1$ as the average or mean relaxation rate. To underline the observation of a slowing down process for $1/T_1$, an Arrhenius plot of the spin–lattice relaxation rate $1/T_1$ at 7.59 MHz/4.6 kOe is given in figure 4(b). The exponential decrease $1/T_1 \propto \exp(-\Delta/T)$ towards lower temperatures is accompanied by a temperature-independent stretching exponent $\beta \approx 0.5$ (see the inset of figure 4) indicating that the exponential change of $1/T_1(T)$ is significant and not due to varying β-values within the stretched-exponential formalism.

In order to check that we had really observed an intrinsic effect indicating the slowing down of $1/T_1$ towards lowest temperatures, we performed additional measurements on a further sample marked as sample #3 (see figure 5). Below 5 K, the ^{7}Li linewidth of sample #3 (solid downward-pointing triangles in figure 5) was enhanced by a factor of 2 compared to the results for sample #1, indicative of a higher concentration of defect spins (see the inset in figure 5). However, $1/T_1(T)$ within the experimental uncertainties followed the results for sample #1, demonstrating the intrinsic character of the slowing down process which is driven by the strong but highly frustrated spin–spin interactions [24]. Rejecting an interpretation in terms of a Kondo compensation, the next plausible explanation clearly would be based on a rather canonical SG transition. The low-temperature maximum in $1/T_1(T)$ and the knee-like structure in the temperature dependence of the heat capacity could be interpreted in terms of a

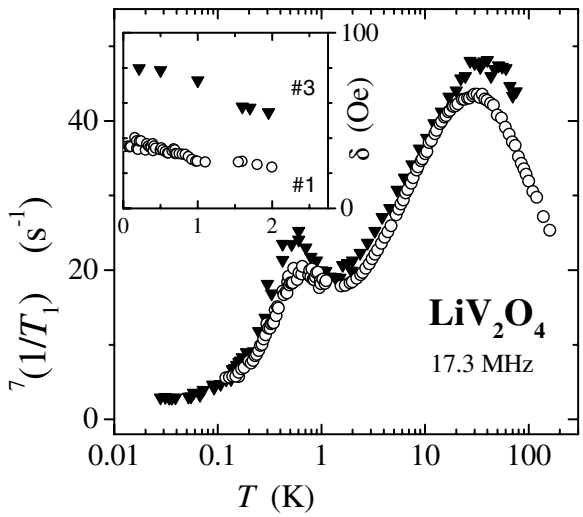

Figure 5. Semi-logarithmic representation of the ^{7}Li spin–lattice relaxation rate $1/T_1$ versus temperature T for LiV_2O_4: sample #1 (○) and sample #3 (▼) at 17.3 MHz/10 kOe. Inset: the temperature dependence of the linewidth δ (FWHM) for both samples.

SG freezing temperature. However, the specific heat in spin glasses exhibits a broad feature at temperatures exceeding the freezing temperature by a factor of 1.3 [25]. This is not in accord with our results which reveal the anomalies in $1/T_1$ and C/T both at approximately 0.6 K. We also would like to mention that a cusp-shaped maximum can still be observed at external fields as high as 10 kOe. In canonical SG, cusp-like anomalies are readily suppressed at fields well below 10 kOe. It has been pointed out by Villain [26] that in the cubic spinel, canonical SG behaviour is unlikely to occur. Of course, a SG transition in LiV_2O_4 could be driven by a small impurity spin concentration. Figure 5 gives some good arguments against this possibility and hence we believe that the low-temperature anomalies are not indications of canonical SG freezing but rather indicate small gap excitations and an intrinsic slowing down of collective spin fluctuations due to geometric frustration.

3. Discussion of the results

Generally, the spin–lattice relaxation rate $1/T_1$ is described via the dynamical susceptibility $\mathrm{Im}\,\chi(q,\omega)$ as [27]

$$T_1{}^{-1} = \frac{\gamma_n^2 k_B T}{2\mu_B^2} A_{\mathrm{hf}}^2 \sum_q \frac{\mathrm{Im}\,\chi(q,\omega,T)}{\omega}. \tag{1}$$

Here A_{hf} is the hyperfine coupling which is assumed to be both isotropic and temperature independent. A Lorentzian-type function is used for the frequency dependence of the dynamical susceptibility:

$$\mathrm{Im}\,\chi(q,\omega) = \chi(q)\frac{\omega\Gamma}{\omega^2+\Gamma^2} \tag{2}$$

where Γ is the magnetic relaxation rate which measures the characteristic energy of the spin-fluctuation spectrum. The prefactor $\chi(q)$ denotes the wave-vector-dependent static susceptibility. In a first approach we neglect any q-dependence of the static susceptibility χ_0.

Under the assumptions outlined above and including a 'metallic' Korringa term, the spin–lattice relaxation rate is given by

$$T_1{}^{-1} = aT + bT\chi_0\frac{\Gamma(T)}{\omega_0^2+\Gamma^2(T)} \tag{3}$$

where $b = \gamma_n^2 k_B A_{\mathrm{hf}}^2/2\mu_B^2$ is a constant and ω_0 gives the radio-frequency of the NMR experiment. The first term takes Korringa-type relaxations into account which stem from contributions of the band states. Using equation (3) the characteristic temperature dependence of the spin–lattice relaxation rate of heavy-fermion systems can be recovered assuming a Curie–Weiss-like susceptibility, $\chi_0 = C/(T+\lambda T^*)$, with $\lambda = \sqrt{2}$ and the characteristic Kondo temperature T^* [28], and a magnetic relaxation rate that reveals the temperature dependence $\Gamma(T) = \delta + \zeta\sqrt{T}$ [29]. Under these simple assumptions, the spin–lattice relaxation rate $1/T_1$ reveals a cusp close to the characteristic temperature $T*$ and a Korringa behaviour with a highly enhanced slope for $T \ll T^*$. These are characteristic features which are observed experimentally in HF compounds [30]. In LiV_2O_4 the temperature dependence of $1/T_1(T)$ nicely resembles this behaviour [2, 3, 13, 22] and the square-root dependence of the magnetic relaxation rate has been proven by means of neutron scattering experiments by Krimmel *et al* [4].

We can easily incorporate the observations made in figure 4 into our model for the spin–lattice relaxation in correlated materials: under the assumption of an exponentially increasing magnetic relaxation $\tilde{\Gamma} = \Gamma(T)\exp(-\Delta/k_BT)$, the spin–lattice relaxation rate $1/T_1$ can be

calculated using equation (3). Below 1 K, the magnetic relaxation rate $\Gamma(T)$ is dominated by the exponential increase, but recovers the square-root dependence at elevated temperatures. In figure 6 we show the results of these model calculations. For these calculations we used a gap value (interaction energy) which depends on the external magnetic field and becomes fully suppressed in external fields $H_{ex} > 44$ kOe. On the basis of these results we conclude that, on decreasing temperature and well below 1 K, the spin fluctuations slow down exponentially. A static spin configuration is reached at $T = 0$ K and at the cusp maximum the measuring frequency ω_0 directly corresponds to the relaxation rate Γ. At temperatures $T \ll 0.6$ K the slow-relaxation regime ($\Gamma \ll \omega_0$) is reached. This observation of a slow spin dynamics down to the lowest temperature is in agreement with the μSR results, where the sample with the lowest impurity concentration revealed a slowing down of spin fluctuations with no signature of static freezing [2, 31].

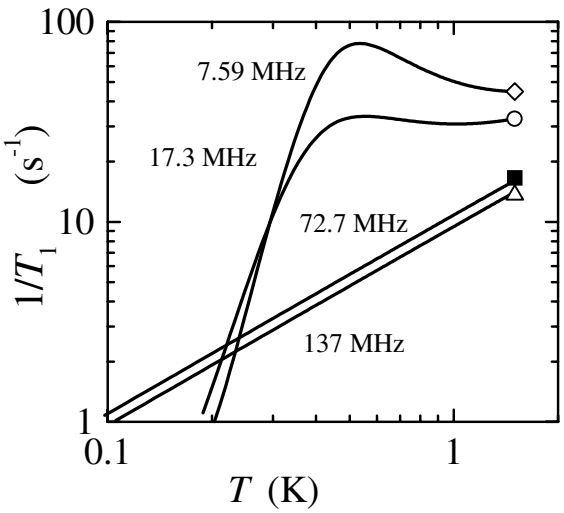

Figure 6. Spin–lattice relaxation rate $\log(1/T_1)$ versus $\log(T)$. The results of model calculations using equation (3) for the measuring frequencies of the NMR experiment and an exponentially increasing magnetic relaxation rate $\tilde{\Gamma}(T) = \Gamma_0 \exp(-\Delta/T)$ with $\Delta = 1.8$ K/7.59 MHz, $\Delta = 1.2$ K/17.3 MHz, $\Delta = 0$ K/72.7 MHz and 137 MHz.

How can these results be reconciled with a HF picture and what is the intrinsic ground state of LiV_2O_4? Of course, LiV_2O_4 is close to magnetic order, since a small degree of Zn doping at Li sites and Ti doping at V sites induces SG freezing [14, 22, 32, 33]. Certainly, the same is true for prototypical HF systems and we would like to recall the case of $CeCu_2Si_2$ which, depending on the exact Ce stoichiometry, reveals superconductivity (the S phase) or magnetic order (the A phase). The regimes of long-range magnetic order and d-wave superconductivity are separated by a phase which is dominated by slow magnetic fluctuations [34]. A variety of different experiments indicate also that the small-moment magnetism in UPt_3 is most probably dynamic in origin. An oscillating spin-density wave, with a characteristic fluctuation rate of some GHz, has been proposed to explain the results on this system [35].

All of these facts reveal striking similarities with the experimental observations on LiV_2O_4. However, LiV_2O_4 should also be compared to canonical spin liquids. It is a frustrated magnet with the V ions forming a lattice of corner-sharing tetrahedra. The spin liquid $Sc_{0.03}Y_{0.97}Mn_2$ reveals the same structural frustration, and has a specific heat coefficient of 160 mJ mol^{-1} K^{-2} and a magnetic relaxation rate of 8 meV. Its striking heavy-fermion-

like behaviour has clearly been addressed [36]. β-Mn is another geometrically frustrated magnet. Also this system reveals no static magnetic order and is characterized by a Sommerfeld coefficient $\gamma = 70$ mJ mol^{-1} K^{-2} and a weakly temperature-dependent magnetic relaxation rate $\Gamma \approx 20$ meV [37].

Spin liquids and heavy fermions reveal very similar dynamical susceptibilities. In both cases, low-lying and usually gapless magnetic excitations govern the dynamic susceptibility. However, the underlying physics seems to be rather different: in spin liquids, long-range magnetic order is suppressed by topological magnetic frustration; soft magnetic excitations are enhanced, favouring the formation of local singlets and the existence of an unconventional non-Néel magnetic ground state [38]. In HF systems, Kondo compensation yields an enhanced density of states at the Fermi energy, driving the formation of heavy quasiparticles. Antiferromagnetic spin fluctuations screen the local moments.

4. Conclusions

What can we conclude for the case of LiV_2O_4? Despite the similarities to observations on Kondo-compensated compounds, we do not believe that Kondo physics gives the appropriate explanation. First of all, it seems that the maximum in $1/T_1(T)$ close to a characteristic temperature $T^* \approx 30$ K and the low-temperature heat capacity cannot be explained on the same footing. A single-ion Kondo model cannot describe the logarithmic increase of $\Delta C/T$ towards low temperatures. In the framework of Moriya's spin-fluctuation theory, the high-temperature anomaly in the spin–lattice relaxation rate gives a characteristic temperature $T_0 = 800$ K [13, 14] while the low-temperature increase of the Sommerfeld coefficient yields $T_0 = 26$ K (figure 2). The heat capacity $\Delta C/T$ towards low temperatures clearly shows the characteristics of NFL phenomena which can be observed close to a QCP. And indeed, LiV_2O_4 certainly is close to a spin-glass QCP [18] (figure 2) and a SG state can be induced by Zn or Ti doping at the lowest level [14, 22, 32, 33]. We believe that magnetic frustration effects dominate, rather than Kondo-type moment compensation, and, viewed from this angle, LiV_2O_4 reveals an extraordinarily high degree of frustration with a Curie–Weiss temperature of the order of 50 K [2] and the lack of magnetic order at least down to 100 mK.

Below 1 K, the spin fluctuations slow down and the Sommerfeld coefficient saturates like $\gamma_0 - \alpha\sqrt{T}$. The slowing down of $1/T_1$ is driven by a characteristic energy of the order of 1 K which depends on the external field. This energy probably corresponds to an average hindering barrier between neighbouring configurations of a highly degenerate ground state. Alternatively, the occurrence of an effective interaction energy Δ could be due to dynamic singlet pairing. This is an interpretation in accord with the 'cooperative paramagnet' which has been proposed by Villain [26] as a possible ground state of cubic spinels: the spins of each tetrahedron form antiparallel pairs, at least on a timescale large compared to that of the inverse NMR frequency ω_0.

From the low-temperature heat capacity and NMR results, we believe that LiV_2O_4 should be characterized as a geometrically frustrated magnet and has to be compared to other systems with moments forming corner-sharing tetrahedra like $Sc_{0.03}Y_{0.97}Mn_2$ [36] or the pyrochlores [39]. Amongst them, it belongs to the group of rare examples of true spin liquids which reach no static spin-ice or SG state down to the lowest temperatures and can be compared directly to the pyrochlore $Tb_2Ti_2O_7$ where no sign of magnetic order has been detected down to 70 mK [40]. We conclude that LiV_2O_4 is a further good candidate for being considered a three-dimensional quantum liquid [41] with a continuous slowing down of the spin dynamics. It has been speculated that in such systems a singlet–triplet gap exists, but with a large number

of low-lying singlet–singlet-like excitations. This would probably explain the exotic behaviour of $\Delta C(T)/T$ which can certainly be reconciled with NFL behaviour. Finally, of course we have to admit that the cusp at 0.6 K might be a trace of a rather canonical SG transition which could be driven by a low impurity level. We put forward some arguments against the possibility of a canonical disorder-driven SG. A final answer can only be given if these experiments are carried out on a high-quality single crystal.

However, in addition to geometric frustration, the mixed valence of the vanadium ions and orbital degrees of freedom may also play an important role. For example, charge fluctuations may suppress any long-range magnetic order. Recently, Fulde *et al* [16] interpreted the large Sommerfeld coefficient in LiV_2O_4 as resulting from excitations of $S = 1/2$ Heisenberg rings and chains. The main ingredients of this model are strong correlations between d^1 and d^2 electrons on an ideal tetrahedral lattice. We hope that our experimental findings can be used to sort out the relevant model functions. But it seems that much more work is needed to elucidate the true ground-state properties of LiV_2O_4.

Acknowledgments

We are grateful to S Kehrein for fruitful discussions. This work was partly supported by the Sonderforschungsbereich 484 of the Deutsche Forschungsgemeinschaft and the BMBF under contract number EKM 13N6917/0.

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