

^7Li NMR studies of $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ and $\text{Li}(\text{V}_{1-y}\text{Ti}_y)_2\text{O}_4$

W. Trinkl, N. Büttgen, H. Kaps, and A. Loidl

Experimentalphysik V, Elektronische Korrelationen und Magnetismus, Institut für Physik, Universität Augsburg, D-86135 Augsburg, Germany

M. Klemm and S. Horn

Experimentalphysik II, Institut für Physik, Universität Augsburg, D86135 Augsburg, Germany

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The mixed crystals $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ and $\text{Li}(\text{V}_{1-y}\text{Ti}_y)_2\text{O}_4$ were investigated using ^7Li NMR. The temperature dependencies of the linewidth Δ , the Knight shift K , the spin-spin relaxation rate $1/T_2$, and the spin-lattice relaxation rate $1/T_1$ were investigated for concentrations $0 \leq x \leq 0.3$ and $0 \leq y \leq 0.2$ in the temperature range from 1.5 K to 280 K. In all samples the magnetization recovery exhibits nonexponential behavior at low temperatures and can be fitted using a stretched exponential function with a stretching exponent $\beta < 1$. At higher doping concentrations all compounds reveal transitions into magnetically ordered phases, most probably into spin-glass states. We discuss the nature of these transitions and the differences between the Zn- and the Ti-doped samples. Even in the pure compound we find deviations from a Korringa behavior due to spin fluctuations. The results are discussed in comparison to prototypical heavy-fermion systems.

I. INTRODUCTION

Stimulated by the observation of high-temperature superconductivity and colossal magnetoresistance effects there is currently great interest in the behavior of transition-metal oxides. In most of these systems correlation and charge-transfer effects have to be considered in degenerate orbitals. New ground-state properties arise due to the interplay of orbital order, Hund's rule coupling, double-exchange interactions, and coupling of the orbital degrees of freedom to the lattice.

At present most work is performed in perovskite-type systems, but there exists a number of old but unresolved questions in compounds with spinel structure. In these compounds the transition metals occupy the sites of a regular tetrahedron and hence they are geometrically frustrated against the evolution of simple antiferromagnetic structures. And indeed most of the spinels are insulating ferrimagnets. However, there exist three metallic spinel-type transition-metal oxides (TMO). Magnetite (Fe_3O_4) may be characterized by the formula $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$, is magnetically ordered below 850 K, and shows a Verwey transition¹ at 118 K, which is even up to now not really understood and has been assumed to be a good candidate for Wigner crystallization. The disappearance of a sharp Verwey transition on doping Fe_3O_4 with fluorine was discussed by Mott in terms of a Wigner glass.² The other two metallic spinel-like TMO are LiTi_2O_4 (Ref. 3) and LiV_2O_4 .⁴ The former is a superconductor³ with a transition temperature as high as 12.5 K, the latter has been reported to be the first heavy-fermion transition-metal oxide.⁵⁻⁷ It is interesting to note that both compounds that reveal the cubic spinel structure are nonmagnetic down to the lowest temperatures, which possibly results from the geometrical frustration and, as outlined above, is an inherent property of the spinel structure where the transition-metal ions form corner sharing tetrahedra. It is also interesting to note that both compounds, like magnetite,

are characterized by a noninteger effective valence of the transition metal. Titanium in LiTi_2O_4 has an effective valence of 0.5 while vanadium in LiV_2O_4 shows a $d^{1.5}$ configuration. On the contrary, ZnV_2O_4 exhibits a d^2 configuration, reveals a slight distortion of the tetrahedra at the cubic to tetragonal phase transition close to 100 K and orders magnetically below 50 K.⁸ The effective valence of V is $(3+x)/2$ for the $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ alloys and on the average is $1.5-y$ per transition metal atom for $\text{Li}(\text{V}_{1-y}\text{Ti}_y)_2\text{O}_4$.

^7Li NMR measurements were the key experiments to identify LiV_2O_4 as a heavy-fermion compound.⁵ Starting at high temperatures, the spin-lattice relaxation rate $1/T_1$ continuously increased on decreasing temperatures. This behavior is commonly observed in compounds that are dominated by spin fluctuations. In LiV_2O_4 the longitudinal relaxation reaches a broad maximum close to 50 K and decreases linearly below 10 K indicating a Korringa type of behavior with a highly-enhanced slope as compared to normal metals. This anomalous Korringa behavior was observed in f -derived heavy-fermion systems and hallmarks a highly enhanced electronic density-of-states at the Fermi energy.⁹ The high density-of-states results from a strong hybridization of the local moments with the conduction electrons. At low temperatures the local moments are completely compensated by the conduction electrons. This Kondo compensation yields high-effective masses of the charge carriers resulting in a high linear term of the specific heat, in a large and temperature-independent Pauli spin susceptibility and in a highly-enhanced Korringa slope.¹⁰ In LiV_2O_4 , the electronic term in the heat capacity was found⁵ to be of the order of 420 mJ/mol K^2 . In $4f$ heavy-fermion systems the electronic mass enhancement is attributed to hybridization effects between the localized $4f$ states and itinerant s, p, d electrons. In LiV_2O_4 hybridization must occur within the t_{2g} bands. Band-structure calculations¹¹⁻¹⁴ have been performed attempting to explain this behavior. Anisimov *et al.*¹² showed

that one $3d$ electron is localized in the A_{1g} orbital while the remaining 0.5 electronic states per V ion form a conduction band mainly of e_g symmetry. In this model the on-site Hund's rule ferromagnetic coupling competes with an inter-site antiferromagnetic exchange and this situation theoretically can be mapped onto a Kondo lattice model.¹² Arguments why the Kondo effect is larger than double exchange have been given by Varma.¹⁵

At the same time NMR experiments were published by Fujiwara *et al.*¹⁶ and were interpreted in terms of a spin fluctuations close to a ferromagnetic instability.¹⁷ Later on, NMR experiments extending to higher temperatures,^{18,19} reporting some ^{51}V results¹⁹ and investigating in detail linewidth and Knight shift effects have been published. NMR experiments in $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ were performed by Amako *et al.*,²⁰ by Fujiwara *et al.*¹⁸ and by Onoda *et al.*²¹ But these experiments mainly focused on the high-temperature properties and did not report on the low-temperature electronic instabilities, reported in this paper.

LiV_2O_4 is an ideal candidate to study the evolution of a heavy fermion ground state by ^7Li NMR measurements, because the lithium atoms are located at a cubic lattice site. Hence only one single line will be observed in the NMR spectra and no quadrupolar effects have to be taken into account. In this manuscript we describe systematic ^7Li NMR investigations of LiV_2O_4 , which were slightly doped with Zn and Ti, where Zn occupies the Li site and Ti substitutes for V. While there exists some data of Zn-doped compounds, to our knowledge, no NMR measurements were performed on Ti-doped samples. In addition, the NMR measurements on the Zn-doped compounds paid special attention to the metal-insulator transition, between the metallic LiV_2O_4 and insulating ZnV_2O_4 . In the present paper, we focus on the low temperatures and low Zn concentrations where heavy-fermion formation competes with the evolution of magnetic order. The appearance of a spin-glass state has been reported by Ueda *et al.*⁸ for Zn concentrations $0.2 < x < 0.8$. In addition we carefully analyzed the recovery of the nuclear magnetization and found significant deviations from a pure exponential behavior indicating the onset of magnetic correlations.

II. EXPERIMENTAL DETAILS

A. Sample preparation

Polycrystalline samples of $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ and $\text{Li}(\text{V}_{1-y}\text{Ti}_y)_2\text{O}_4$ were prepared by sintering a mixture of powders of LiV_2O_3 , ZnV_2O_3 , LiTi_2O_3 , and VO with a slight excess of LiV_2O_3 in order to compensate for Li evaporation. Platinum crucibles were used for the reaction of the powders at 750°C for 10 days. In x-ray diffraction experiments we found the nominally pure fcc spinel structure. A detailed study of lattice constants and magnetization measurements, which are the key experiments to look for sample quality,²² will be published elsewhere.

B. NMR Measurements

The experiments were carried out using a phase-coherent pulse spectrometer with field sweeps at a constant frequency of 17.3 MHz. For ^7Li (nuclear spin $I=3/2$, gyromagnetic

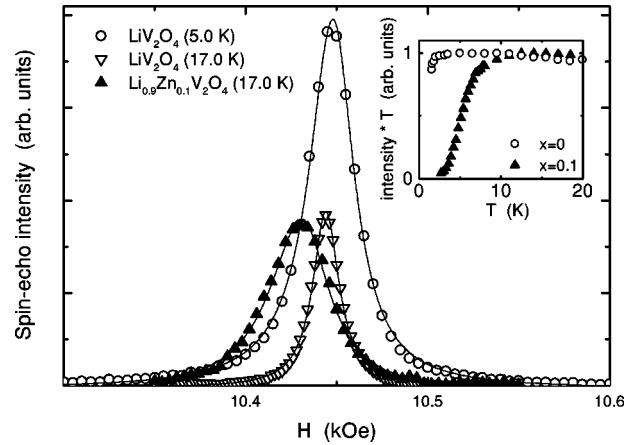


FIG. 1. ^7Li field-sweep spectra of LiV_2O_4 (open circles: 5 K, open triangles: 17 K) and $\text{Li}_{0.9}\text{Zn}_{0.1}\text{V}_2\text{O}_4$ (closed triangles: 17 K). The spectrometer frequency was 17.3 MHz. The inset shows the temperature dependence of the product of spin-echo intensity \star temperature.

ratio $\gamma=16.546$ MHz/T) we perform measurements of the linewidth Δ , the Knight shift K , the spin-spin relaxation rate $1/T_2$, and the spin-lattice relaxation rate $1/T_1$. The spectra were collected using a conventional $\pi/2 - \tau_D - \pi$ spin-echo sequence. The linewidth Δ was deduced from the field-sweep spectra taking the full width at half-maximum. For T_2 measurements, determining the spin-spin relaxation time, the spin-echo pulse sequence was applied with variable pulse spacing τ_D . T_2 was determined by fitting the exponential decrease of the intensity plotted vs $2\tau_D$. The spin-lattice relaxation rate $1/T_1$ was determined from the recovery of the spin-echo intensity after an inversion pulse waiting about five times T_1 between each inversion pulse sequence. Depending on doping concentrations pulse lengths have been chosen, which irradiate the entire spectral line, a condition that only has been violated in some exceptional cases, close to anomalies in $\Delta(T)$.

III. RESULTS

A. Line shape and Knight shift

Some representative results of the ^7Li spectra are shown in Fig. 1. The Li nucleus is characterized by a spin $I=3/2$ and as a consequence of the cubic lattice site, only one single line is observed. The spectra are almost symmetric and can reasonably be described using a Lorentzian line shape (solid lines in Fig. 1). No electric-field gradient splits or broadens the line in the powdered samples. In the pure compound the intensity increases with decreasing temperature and the linewidth slightly broadens. The inset in Fig. 1 shows the product of intensity and temperature (IT) and reveals that in the pure compound the intensity follows a Curie-like behavior down to the lowest temperatures. In the Zn-doped compound the line is already broad at elevated temperatures. This observation signals that the linewidth Δ reflects the strength of spin fluctuations and most probably the closeness to a transition into a magnetically or electronically ordered state for $x>0.05$. This conclusion is corroborated by the fact that lifetime broadening of the nuclear-nuclear interaction does

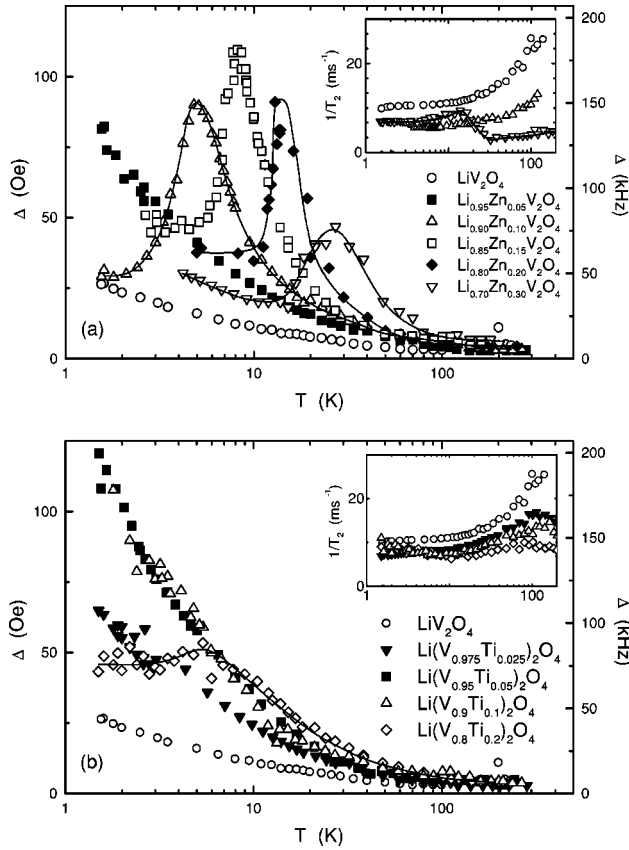


FIG. 2. Temperature dependence of the ^7Li linewidth Δ in $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ (a) ($x=0$: open circles, $x=0.05$: closed squares, $x=0.1$: open triangles up, $x=0.15$: open squares, $x=0.2$: closed diamonds, $x=0.3$: open triangles down) and $\text{Li}(\text{V}_{1-y}\text{Ti}_y)_2\text{O}_4$ (b) ($y=0$: open circles, $y=0.025$: closed triangles down, $y=0.05$: closed squares, $y=0.1$: open triangles up, $y=0.2$: open diamonds) in field (left scales) and frequency units (right scales), respectively. The insets show the temperature dependence of the spin-spin relaxation rate $1/T_2$. The solid lines are drawn to guide the eye.

ot effect the linewidth as is indicated by the monotonous decrease of the spin-spin relaxation rate $1/T_2$ towards low temperatures [see the insets of Figs. 2(a) and 2(b)]. A steep decrease in the intensity (inset of Fig. 1) indicates a transition into a low-temperature state with an ordered or frozen spin configuration. At the lowest temperatures only a small fraction ($<5\%$) of nuclear spins contribute to the total NMR intensity.

The temperature dependence of the linewidth Δ for all compounds investigated is shown in Figs. 2(a) ($\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$) and 2(b) [$\text{Li}(\text{V}_{1-y}\text{Ti}_y)_2\text{O}_4$]. Focusing on the pure compound, the linewidth continuously increases on decreasing temperatures reaching values close to 25 Oe corresponding to 41 kHz at 1.5 K. This linewidth is slightly larger compared to the linewidths obtained from Fourier transform of the time domain by Mahajan *et al.*¹⁹ in their best LiV_2O_4 samples (20 kHz–30 kHz) and documents a comparable sample quality. At higher temperatures the linewidth approaches the same value for all samples [Figs. 2(a) and 2(b)] indicating that there is no broadening of the line due to nonmagnetic inhomogeneities and sample quality. With increasing Zn doping the increase towards low temperatures strongly increases and reveals a maximum close to

5 K ($x=0.1$), 8 K ($x=0.15$), 12 K ($x=0.2$), and ~ 25 K ($x=0.3$). For the Ti-doped samples one observes a strong increase towards lower temperatures for $0.025 \leq y \leq 0.1$. For $y=0.2$ this continuous increase levels off towards a constant value at about 8 K. Contrary to the Zn-doped compounds no maxima were observed for the Ti concentrations under investigation. We recall, that for $x > 0.05$, concomitantly with the decrease of the linewidth, the signal intensity strongly decreases (see the inset of Fig. 1). This behavior signals the freezing of local spins. The nuclei that are lost reside in regions with frozen spin configurations and strong local fields that in turn produce a large and inhomogeneous linewidth due to a distribution of internal fields. The remaining signal comes from spins that are not embedded in clusters and still can relax freely. This behavior is expected close to a spin-glass or magnetic transition and has been described in prototypical spin glasses like Cu:Mn .²³

The spin-spin relaxation rate $1/T_2$ decreases continuously towards low temperatures and no anomalies corresponding to the onset of magnetic order could be observed for all samples with $x < 0.1$ and $y < 0.2$ [see insets of Figs. 2(a) and 2(b)]. For $x \geq 0.1$ [inset in Fig. 2(a)] and for $y = 0.2$ [inset in Fig. 2(b)] an increase of $1/T_2$ was detected with an onset temperature corresponding to the anomalies in $\Delta(T)$. This also clearly shows that the broadening of the linewidth Δ is not affected by a reduction of the spin-spin relaxation rate, which decreases for increasing doping concentration for all temperatures.

The Knight shift measures the local static susceptibility and local electronic density-of-states. The temperature dependence of the Knight shift for all compounds investigated is shown in Figs. 3(a) and 3(b). The Knight shift in pure LiV_2O_4 reveals a broad cusp close to 40 K and a smooth decrease down to lowest temperatures, similar to the published results by Kondo *et al.*,⁵ Mahajan *et al.*,¹⁹ and Fujiwara *et al.*¹⁸ On increasing Zn concentration, the maximum shifts to lower temperatures, and the Knight shift reveals an abrupt decrease at the transition temperatures, as indicated by $\Delta(T)$. On increasing Ti concentration, again the maximum shifts to lower temperatures on increasing Ti doping. A sharp anomaly appears for $y=0.2$ at $T \sim 11$ K. This is exactly the temperature where Δ levels off [Fig. 2(b)] and $1/T_2$ reveals a slight increase [inset of Fig. 2(b)].

B. Spin-lattice relaxation

The spin-lattice relaxation rate was measured using an inversion recovery pulse sequence. The magnetization recovery was almost exponentially at elevated temperatures, however, deviated significantly at low temperatures and for higher-doping levels. We tried to fit the magnetization recovery using a stretched exponential behavior

$$M(t) = A \exp[-(t/T_1)^\beta] \quad (1)$$

with a stretching exponent β that depends on temperature and doping concentration. Such a relaxation is expected for a system with nonrandom fluctuations, where β describes the degree of correlation. In the present case a transition into a spin-glass state with a distribution of spin-lattice relaxation times due to different local relaxation channels with different T_1 , is the most plausible explanation. In the latter case the parameter β is a measure of the width of the distribution,

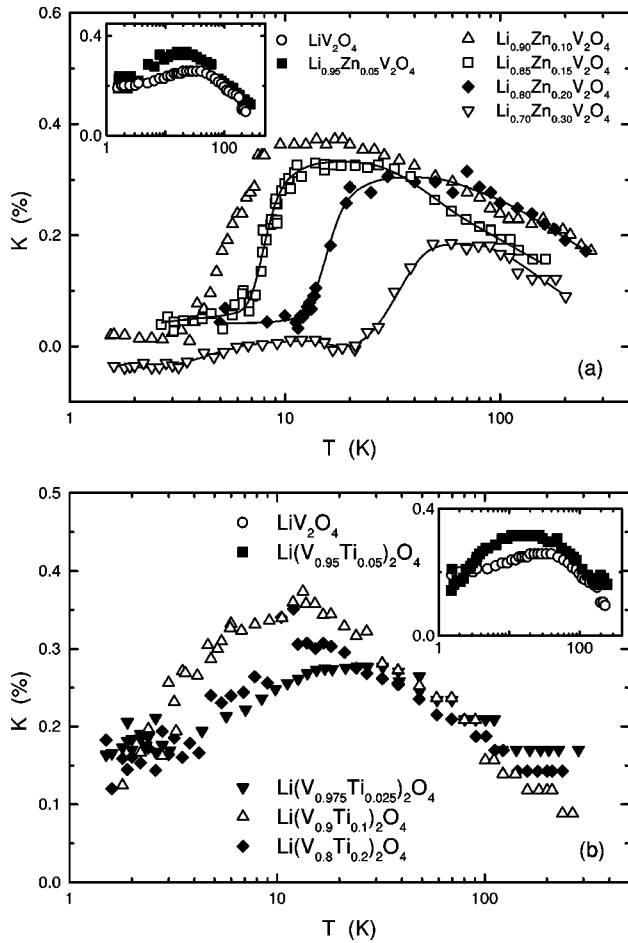


FIG. 3. Temperature dependence of the ${}^7\text{Li}$ Knight shift in $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ (a) ($x=0.1$: open triangles up, $x=0.15$: open squares, $x=0.2$: closed diamonds, $x=0.3$: open triangles down) and $\text{Li}(\text{V}_{1-y}\text{Ti}_y)_2\text{O}_4$ (b) ($y=0.025$: closed triangles down, $y=0.1$: open triangles up, $y=0.2$: closed diamonds) at higher doping levels. The solid lines are drawn to guide the eye. The insets show $K(T)$ for pure LiV_2O_4 (open circles), and for samples with $x=0.05$ (closed squares) and $y=0.05$ (closed squares), respectively.

which could be explained with a spin-glass like state due to a frustrated antiferromagnetic order. These two different behaviors cannot be distinguished²⁴ experimentally. Results of the fitting procedure over almost four decades in the pulse separation time are given in Fig. 4 and corresponding values are displayed in Table I. A stretched exponential behavior allows to fit the whole magnetization curve (see solid lines in Fig. 4) instead of fitting only a small region where exponential behavior holds, but a lot of information is lost (see dotted lines in Fig. 4). From the values of the spin-lattice relaxation rate $1/T_1$ as given in Table I, it is clear that there is reasonable agreement for the two different fitting procedures, when the β parameter is close to unity, but the deviations increase dramatically with decreasing β , in which case a pure exponential behavior is unable to describe the magnetization recovery. We conclude that a careful analysis of T_1 is important to check whether relaxation rates obtained from stretched exponential fits will yield a Korringa behavior at low temperatures. To decide this open question the measurements should be extended towards lower temperatures.

The temperature dependencies of the stretching exponent

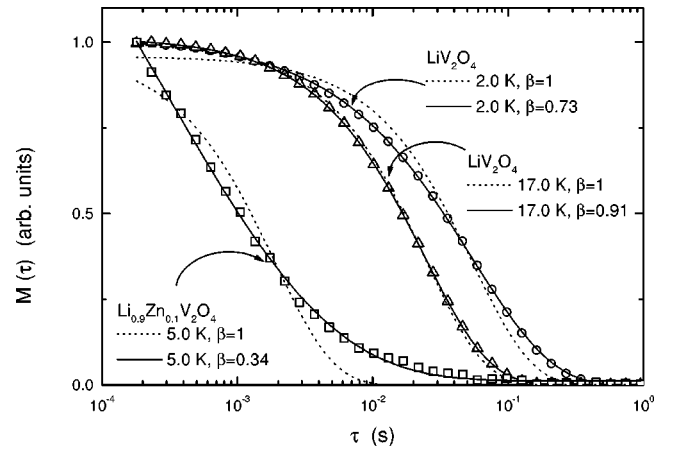


FIG. 4. Magnetization recovery vs pulse separation time τ . Best fits in LiV_2O_4 (open circles: 2 K, open triangles up: 17 K) and in $\text{Li}_{0.9}\text{Zn}_{0.1}\text{V}_2\text{O}_4$ at 5 K (open squares) with a stretched exponential function $M(\tau) \propto \exp[-(\tau/T_1)^\beta]$ with $0 < \beta < 1$, are indicated as solid lines. Fits with a purely exponential function ($\beta=1$) are drawn as dashed lines. The data were normalized to unity at the shortest time.

β are displayed in Fig. 5 for the Zn (a) and Ti (b) samples. Above 30 K all magnetization recovery clearly is very close to a purely exponential behavior and no differences between the different samples could be observed. However, significant deviations appear at low temperatures that become increasingly strong at higher-doping concentrations, where β can be interpreted as a precursor of a spin-glass transition. At 1.5 K, the stretching exponent becomes 0.7 in the pure compound, but reaches values of almost 0.2 close to the freezing transition in the compounds with $x=0.1$, $x=0.15$, and $x=0.2$. Well below the freezing temperatures, the stretching exponent in the doped compounds levels off at a constant value close to $\beta=0.5$. For the Ti-doped samples no sharp anomaly could be observed and there is only a smooth decrease to $\beta=0.5$. A nonexponential recovery is expected if the nuclei relax in disordered systems. A stretching exponent of $\beta=0.5$ typically is observed in dilute nuclear systems with a vanishingly small spin-diffusion coefficient.²⁵ Also impurities are able to produce a stretched exponential behavior,²⁶ but in this case no strong temperature dependence should be observed and the dependence on impurity concentration should be more important as is the case in our samples. We recall that in the doped samples under investigation and at the lowest temperatures, only a small fraction of spins contribute to this signal. These spins relax independently in random fields caused by the surrounding frozen-in spin configuration. A similar behavior was found in CeAl_3 ,²⁷ where the magnetization recovery could well be fitted by a

TABLE I. Comparison of the different fitting functions as explained in the text. $1/T_1$ is the rate from the stretched exponential fit, and $1/T_1^{\text{mono}}$ is the rate deduced from a simple monoexponential ($\beta=1$) fit, respectively.

		β	$1/T_1$	$1/T_1^{\text{mono}}$
LiV_2O_4	2 K	0.73	18.4	19.5
LiV_2O_4	17 K	0.91	41.2	41.4
$\text{Li}_{0.9}\text{Zn}_{0.1}\text{V}_2\text{O}_4$	5 K	0.38	3930	614

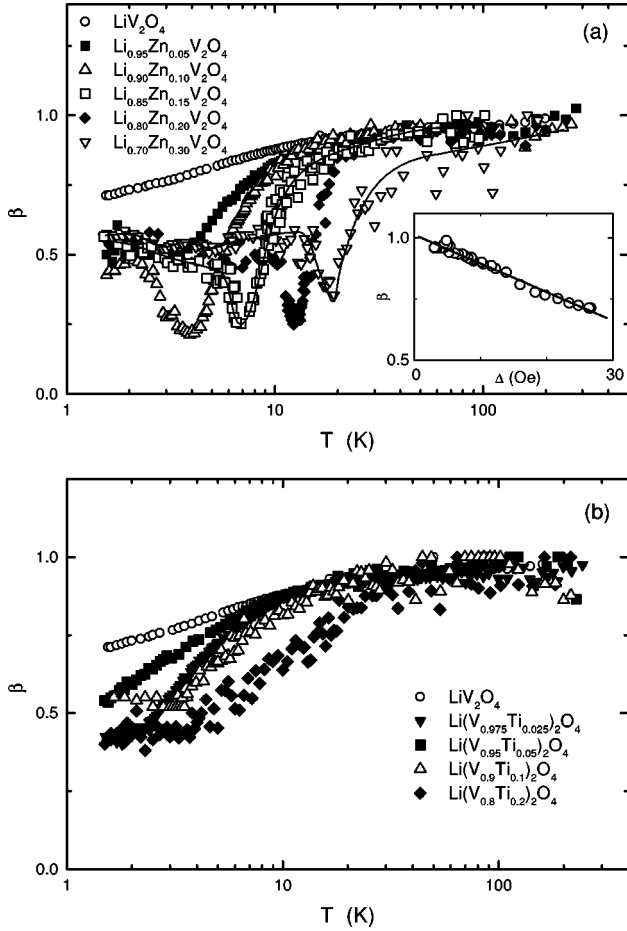


FIG. 5. Temperature dependence of the stretching exponent β in $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ (a) ($x=0$: open circles, $x=0.05$: closed squares, $x=0.1$: open triangles up, $x=0.15$: open squares, $x=0.2$: closed diamonds, $x=0.3$: open triangles down) and $\text{Li}(\text{V}_{1-y}\text{Ti}_y)_2\text{O}_4$ (b) ($y=0$: open circles, $y=0.025$: closed triangles down, $y=0.05$: closed squares, $y=0.1$: open triangles up, $y=0.2$: closed diamonds). The inset in (a) shows the stretching exponent β vs the linewidth Δ as observed in pure LiV_2O_4 .

sum of an exponential and a nonexponential behavior with an exponent $\beta=0.5$. This behavior was interpreted in terms of a magnetically inhomogeneous ground state, where a paramagnetic fraction of the sample relaxes monoexponentially, while the spins in the remaining part relax with a stretching exponent $\beta=0.5$. It was assumed that this second phase does not order magnetically, but rather is dominated by intersite correlations of fluctuating cerium moments. The existence of a second phase was corroborated by a broad underlying pattern evolving for temperatures below 3 K.²⁷ In sharp contrast we cannot detect a fingerprint of a second phase in the spectra of our samples. Additionally, fitting our relaxation data with a sum of monoexponential and stretched exponential contributions yields rather poor results only. It is shown in the inset of Fig. 5(a) that β and Δ are intimately connected via a linear dependence, indicating a common origin of the temperature dependence of these two parameters.

Figures 6(a) and 6(b) show the temperature dependence of the spin-lattice relaxation rates for the pure and the doped compounds. On decreasing temperatures, in pure LiV_2O_4 , $1/T_1$ slightly increases, passes through a maximum close to

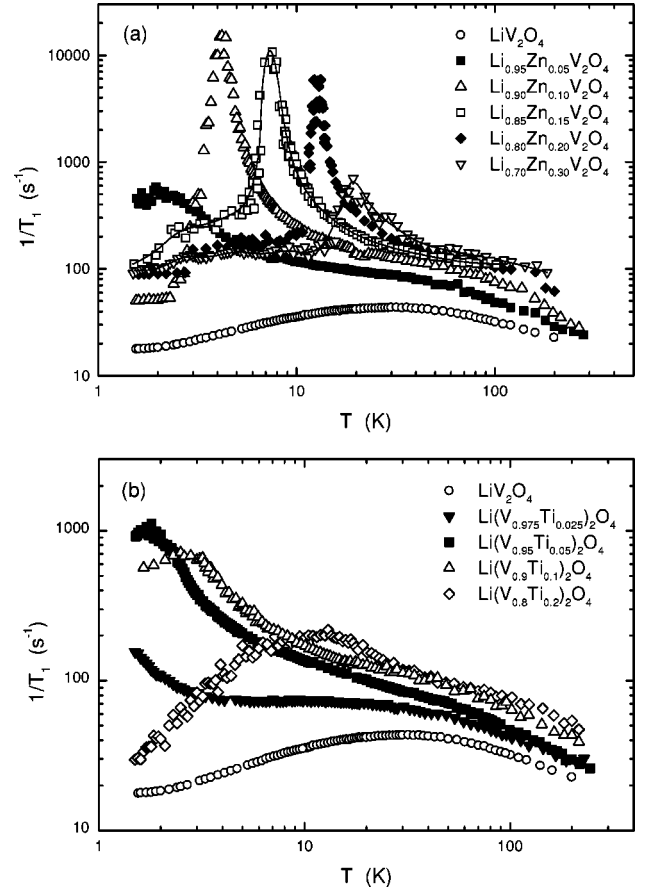


FIG. 6. (a) Spin-lattice relaxation rate ($1/T_1$) vs temperature T in $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ (a) ($x=0$: open circles, $x=0.05$: closed squares, $x=0.1$: open triangles up, $x=0.15$: open squares, $x=0.2$: closed diamonds, $x=0.3$: open triangles down) and $\text{Li}(\text{V}_{1-y}\text{Ti}_y)_2\text{O}_4$ (b) ($y=0$: open circles, $y=0.025$: closed triangles down, $y=0.05$: closed squares, $y=0.1$: open triangles up, $y=0.2$: open diamonds). The strong anomalies [see (a)] at temperatures $T=4$ K ($x=0.1$) and $T=12$ K ($x=0.2$) coincide with anomalies in linewidth Δ , Knight shift K , and stretching exponent β at identical temperatures. The solid lines are drawn to guide the eye.

30 K, and decreases towards the lowest temperatures. No indications of a structural or magnetic phase transition were observed. The maximum value of approximately $1/T_1=40$ s⁻¹ agrees well with the values reported in the literature.^{5,18,19} However, the decrease towards low temperatures is definitely much weaker than linear as it has been observed by Kondo *et al.*⁵ where the linear temperature dependence was one of the key properties to classify LiV_2O_4 as a heavy-fermion system. In the slightly doped compound, with $x=0.05$, the first plateau at $T\sim 30$ K, which corresponds to the maximum in pure LiV_2O_4 , is followed by a second increase towards low temperatures. For $x=0.1$, $x=0.15$, and $x=0.2$ a sharp anomaly in $1/T_1(T)$ corresponds to the anomalies in $\Delta(T)$ most probably indicating a transition into a frozen-spin configuration. Similar observations are made for $y>0$, but no sharp anomalies could be observed in these compounds. A second broad maximum evolves for $y=0.2$ followed by an almost linear (Korringa-like) decrease towards the lowest temperatures. The temperature dependence of the spin-lattice relaxation rate for $y>0.2$ are similar to the findings in the magnetically ordered heavy-fermion system CeAl_2 .³⁰ But the anomaly in

$\text{Li}(\text{V}_{0.8}\text{Ti}_{0.2})_2\text{O}_4$ is definitely broader and appears to be smeared out indicative for a spin-glass transition.

IV. DISCUSSIONS AND CONCLUSIONS

In starting this section we briefly want to summarize the most important results of this ^7Li NMR investigation of $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ and $\text{Li}(\text{V}_{1-y}\text{Ti}_y)_2\text{O}_4$: The linewidth in all compounds increases on decreasing temperatures, an effect that significantly becomes enhanced in Zn-, as well as in Ti-doped compounds. The linewidth broadening certainly results from magnetic fluctuations, due to the fact that at the same time the spin-spin relaxation rate decreases in all systems. Well-defined and rather sharp anomalies show up for the compounds with $x=0.1$ ($T=5$ K), 0.15 ($T=8$ K), 0.2 ($T=10$ K), and 0.3 ($T=30$ K). Below these characteristic temperatures the linewidth steeply decreases. In clear contrast, for the compound with $y=0.2$, $\Delta(T)$ levels off at a constant value below 5 K. For all alloys with lower doping levels the linewidth smoothly increases down to the lowest temperatures of this investigation (1.5 K). At the highest-doping levels the anomalies in $\Delta(T)$ are accompanied by a steplike increase of the spin-spin relaxation rate $1/T_2$ [insets of Figs. 2(a) and 2(b)]. It is straightforward to assign these anomalies to the occurrence of magnetic instabilities most probably a spin-glass state. The Knight shift $K(T)$, in all compounds is positive, has a cusplike shape, and reaches values up to 0.4% in the broad maximum. The maxima of $K(T)$ decrease on increasing concentration, however, a sharp drop in the temperature dependence appears at the onset of magnetic order for the Zn-doped compounds, while the cusplike shape remains smooth for all Ti-substituted vanadates. The recovery of the spin-echo intensity becomes significantly nonexponential at low temperatures and can well be fitted assuming a stretched exponential function. The intensity of the signal drops strongly below the transition temperatures T_M , and already at $T_M/2$ only less than 10% of the nuclear spins contribute to the signal (see, e.g., inset of Fig. 1). These spins relax independently in random fields as documented by a stretching exponent $\beta=0.5$. The majority of the nuclear spins is embedded in regions with static spin order and do not contribute to the spin-echo intensity. This behavior prototypically is observed in magnetic systems revealing long- or short-range magnetic order. In almost all doped samples the stretching exponent tails off at a value of $\beta=0.5$, which is the limiting value of systems without spin diffusion. Finally, the spin-lattice relaxation rates $1/T_1(T)$ for all alloys are shown in Figs. 6(a) and 6(b). In good agreement with the findings in $\Delta(T)$ and $K(T)$, sharp and peak-like anomalies were detected for $x=0.1$, 0.15 , 0.2 , and 0.3 , while only a smooth, smeared-out cusp appears for $y=0.2$. In the pure compound LiV_2O_4 , the spin-lattice relaxation rate increases on decreasing temperatures, passes through a broad maximum close to 30 K, and decreases for further decreasing temperatures, but never reaches pure Korringa behavior in the samples under investigation.

Before discussing the experimental evidence of this investigation for heavy-fermion formation we would like to quantify the strength of magnetic correlations. We tried to fit the temperature dependent linewidth Δ using

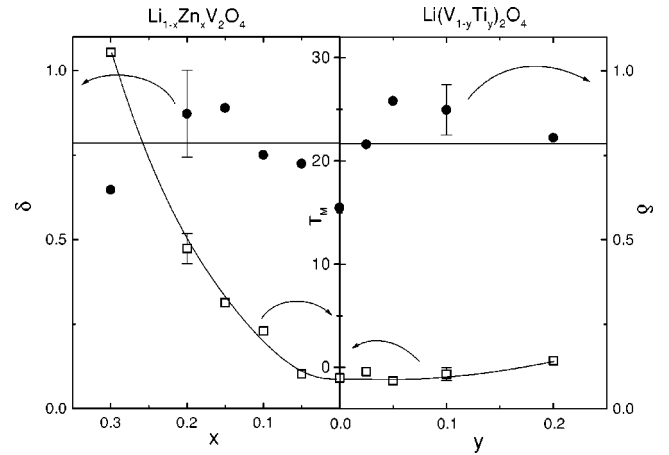


FIG. 7. Magnetic ordering temperatures T_M (middle scale) and “critical exponents” δ (left and right scale) vs x and y . T_M and δ have been determined as described in the text. The solid lines are drawn to guide the eye.

$$\Delta = A/(T - T_M)^\delta. \quad (2)$$

A is a constant, T_M the critical temperature, and δ is treated like a critical exponent. From a theoretical point of view a similar fit to $1/T_1(T)$ seems to be more meaningful. However these fits can be performed on some samples only, while fits to $\Delta(T)$ can be performed throughout the complete series of Ti and Zn concentrations.

The results of these fits for all concentrations x and y are given in Fig. 7. With increasing Zn concentration the transition temperatures increase continuously. Below 5% Zn or Ti, T_M is slightly negative but close to 0 K. The exponent δ reveals values between 0.6 and 0.8. The size of the critical exponent is not known for the temperature dependence of the linewidth. However, if we assume that δ is related to the critical exponent ν , which characterizes the growth of the correlation length for $T > T_M$, we note that for three-dimensional Ising model $\nu=0.64$ and for the $d=3$ Heisenberg model a critical exponent $\nu=0.7$ is expected.²⁸ Figure 7 provides experimental evidence that spin fluctuations strongly increase on increasing x , but remain weak for increasing y . Again we have to caution that an analysis of $\Delta(T)$ in terms of critical exponents is a mere parametrization of experimental results.

It is clear from low-temperature spin-lattice relaxation that we do not observe a Korringa law below 5 K as has been found by Kondo *et al.*,⁵ despite the fact that from the NMR linewidth, magnetic susceptibility, and heat capacity²⁹ measurements, the sample quality is similar to those samples investigated in the work of Kondo *et al.*,⁵ Johnston,³ and Fujiwara *et al.*¹⁸ The slight curvature of $1/T_1(T)$ at the lowest temperatures may signal the occurrence of a magnetic (spin) or electronic (charge or orbital degrees of freedom) phase transition below 1 K. Most probably spin freezing occurs at the lowest temperatures. Evidence for a dynamical slowing down has also been observed by Kondo *et al.*⁵ in the purest samples. However, they still obeyed strictly a Korringa-like behavior of $1/T_1(T)$ for $T > 1.5$ K. The sensitivity of the ground-state properties on the fine tuning of the structural properties was also observed in the prototypi-

cal heavy-fermion CeCu_2Si_2 and this will be discussed in the following.

In this section we would like to compare the observations in LiV_2O_4 with experimental findings in prototypical f -derived heavy-fermion systems. It is well known that the spin-lattice relaxation in heavy-fermion compounds reveals a Curie-Weiss-like increase at higher temperatures, passes through a maximum, and decreases linearly at the lowest temperatures with a highly enhanced Korringa rate due to the high-density of electronic states at the Fermi level. The temperature of the cusp maximum roughly gives an estimate of the characteristic temperature T^* , the so-called Kondo lattice temperature.³¹ The prototypical heavy-fermion compound CeCu_2Si_2 with a characteristic temperature of $T^* \approx 15$ K is very close to a magnetic instability and depending on the exact stoichiometry and the growth procedures, a superconducting (S phase: $T_c = 0.6$ K) or a magnetic (A phase: $T_A = 1$ K) ground state is established.^{32,33} The nature of the magnetic ground state still has to be resolved. Ishida *et al.*³⁴ performed a detailed Cu nuclear quadrupole resonance study of CeCu_2Si_2 in its S and A phase. For $T > T_c$ the superconducting samples revealed the temperature dependence of the spin-lattice relaxation rate characteristic for heavy-fermion systems. However, in the A phase crystals, a true Korringa regime never was reached and at low temperatures $1/T_1 T$ is not constant but slightly enhanced. In A phase crystals also the intensity ratio, IT , continuously decreases at the lowest temperatures, as observed in the doped samples of our investigation. No detailed reports on Knight shift and linewidth are available for the heavy-fermion compounds and clear maxima in the Knight shift were only observed in materials with rather high-characteristic temperatures T^* , namely, in CeSn_3 with a characteristic temperature of $T^* = 150$ K (Ref. 35) and in URu_2Si_2 with $T^* = 70$ K.³⁶ In both compounds the maxima in $K(T)$ roughly correspond to the Kondo-lattice temperatures T^* . In URu_2Si_2 , which exhibits a spin-density wave transition at $T_N = 17$ K, the Knight shift levels off at a constant value below T_N . This is not what we observe for the pure and Zn-doped compounds. In these samples $K(T)$ strongly decreases below the (magnetic) ordering temperature [Fig. 3(a)]. Guided by $1/T_1(T)$ and $K(T)$ it seems quite natural to characterize LiV_2O_4 as a heavy-fermion compound very close to magnetic order and with a characteristic temperature of $T^* = 30$ K. Like in CeCu_2Si_2 , the ground-state properties depend on the fine tuning of the sample-preparation procedure. It seems that the pure sample of this investigation orders magnetically (electronically) well below 1 K, which quite naturally explains the deviations from a Korringa relaxation for temperatures $T < 10$ K. On the other hand it seems that the sample investigated by Kondo *et al.*⁵ remains in a pure and coherent nonmagnetic heavy-fermion state. However, as can be seen from the temperature dependence of the linewidth (Mahajan *et al.*¹⁹) spin fluctuations also play an important role in their sample.

The doped compounds most probably undergo spin-glass transitions for $x \geq 0.2$ at low temperatures. Spin-glass behav-

ior has been established in $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ by Ueda *et al.*⁸ The glass transition temperatures in our samples seem to be slightly enhanced as compared to the magnetization results from Ueda *et al.*,⁸ where the difference between field-cooled and zero-field-cooled magnetization was used to determine the freezing temperatures (here the value for T_f depends on the exact measurement procedure) and to identify the samples as spin glasses. However, our experiments have been directed in external magnetic fields of approximately 1 T, which may explain these discrepancies. But we would like to point out that both the very sharp anomalies in the temperature dependencies of the linewidth, Knight shift, and spin-lattice relaxation rate as observed for the Zn-doped compounds, are rather unusual when compared to conventional spin-glass systems. Also the drop in the quantity IT is drastically stronger as observed in spin glasses. It is also much larger as observed in A phase crystals of CeCu_2Si_2 .³⁴ The experimental results in the Ti samples to a large extent are fingerprints of a spin-glass transition. However, there the observation of a broad cusp for $y = 0.2$ in $1/T_1(T)$ with a subsequent strongly enhanced Korringa law [Fig. 6(b)] is rather unusual and calls for further investigations.

Of course at first sight the occurrence of a spin-glass transition in pure LiV_2O_4 seems most plausible. However a spin-glass configuration is rather astonishing due to the fact that the characteristic temperature T^* of LiV_2O_4 is close to 30 K (obtained from the cusp in the temperature dependence of the Knight shift and of the spin-lattice relaxation rate): At this characteristic temperature, moment compensation occurs and probably would be fully completed below $T^*/10$ as is the case in traditional heavy-fermion systems. It is also unclear how spin-glass behavior can occur in a completely stoichiometric compound, but at this point the geometrical frustration may come into play. In addition, the observation of a pure and stoichiometric heavy-fermion spin-glass has been reported recently.³⁷ Another possibility could be an itinerant picture that all spin degrees of freedom have been transferred into the band states and at low temperatures a heavy-fermion band magnetism becomes established.^{38,31}

Despite these nonresolved problems and open questions the appearance of a probably unusual spin-glass state in $\text{Li}_{1-x}\text{Zn}_x\text{V}_2\text{O}_4$ and $\text{Li}(\text{V}_{1-y}\text{Ti}_y)_2\text{O}_4$ seems most plausible. But we would like to recall that systems with a broken number of electrons per transition metal site (1.5 electrons per V site in the pure compound) are unstable against charge order transitions, as is well known from the spinel-type compound magnetite and from the doped perovskite manganates. From the band-structure calculations¹¹⁻¹³ LiV_2O_4 also reveals orbital degeneracy and certainly also the orbital degrees of freedom may play an important role for the ground-state properties.

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